Cellulose Fiber Reinforced Nylon 6 or Nylon 66 Composites

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CELLULOSE FIBER REINFORCED NYLON 6 OR NYLON 66 COMPOSITES

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To my husband Yi Liu and my son, Kevin

And

To my parents Jingshan Xu and Meizhi Zhang

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SUMMARY

Cellulose fiber was used to reinforce higher melting temperature engineering thermoplastics, such as nylon 6 and nylon 66. The continuous extrusion - direct compression molding processing and extrusion-injection molding were chosen to make cellulose fiber/nylon 6 or 66 composites. Tensile, flexural and Izod impact tests were used to demonstrate the mechanical properties of the composites. The continuous extrusion-compression molding processing can decrease the thermal degradation of cellulose fiber, but fiber doesn't disperse well with this procedure. Injection molding gave samples with better fiber dispersion and less void content, and thus gave better mechanical properties than compression molding.

Low temperature compounding was used to extrude cellulose fiber/nylon composites. Plasticizer and a ceramic powder were used to decrease the processing temperature. Low temperature extrusion gave better mechanical properties than high temperature extrusion. The tensile modulus of nylon 6 composite with 30 % fiber can reach 5GPa; with a tensile strength of 68MPa; a flexural modulus of 4GPa, and a flexural strength of 100MPa. The tensile modulus of nylon 66 composites with 30 %fiber can reach 5GPa;with a flexural modulus of 5GPa; a tensile strength of 70MPa; and a flexural strength of 147MPa.

The effect of thermal degradation on fiber properties was estimated. The Halpin-Tsai model and the Cox model were used to estimate the composite modulus. The Kelly-Tyson model was used to estimate the composite strength. The result indicates that the change of fiber properties determines the final properties of

composites. Fiber length has a minor affect on both modulus and strength as long as the fiber length is above the critical length.

CHAPTER 1

BACKGROUND/MOTIVATION

1.1 Background/Motivation

Wood/natural fiber reinforced composites are experiencing rapid growth due to the following advantages over traditional reinforcing agents: (1) renewable and environmentally friendly, (2) low density, (3) low cost, (4) non-abrasive, (5) safe fiber handling, and (6) high specific properties. The demand of natural/wood fiber-plastic composites has enjoyed significant double-digit growth since the early 1990s in north America and Europe (Figure 1.1).[1] The market in North America includes automotive, building, appliance and other applications.

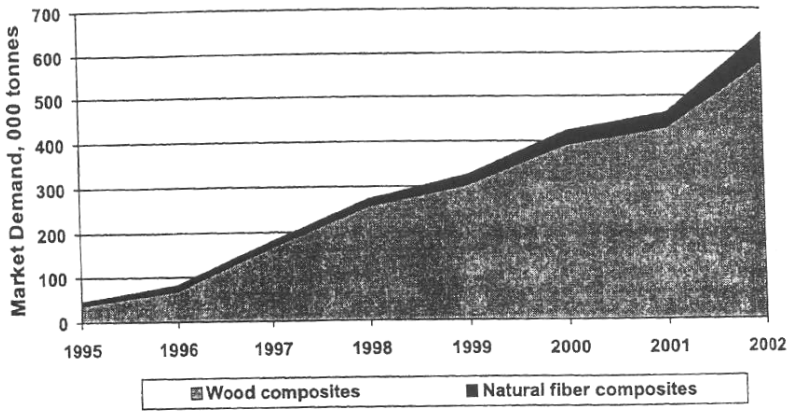

Figure 1.1 Demand for natural and wood fiber-plastic composites, North American and Europe [1]

One primary drawback of the use of wood/natural fiber is the low processing temperature permissible due to the thermal degradation. The common belief is that natural fiber is only suitable for low melting commodity thermoplastics (under 180°C) such as PE, PP, PVC and PS.

Higher melting temperature engineering thermoplastics, such as nylon 6 and nylon 66, have higher modulus and service temperature than commodity thermoplastics. The automotive and constructive market needs the low density reinforcement for engineering thermoplastics to get higher strength, higher modulus, and lower density materials. Purified cellulose from wood fiber is more thermally stable than other constituents, such as lignin and hemicellulose, so it has the potential to be used as a reinforcement of engineering thermoplastics. However, early studies on cellulose fiber reinforced polyamide were generally discouraging. Cellulose fiber exhibited severe degradation when PA 6 was used (melting temperature 220°C) and showed poor reinforcing potential [2].

The main objective of this research is to develop a method to process low cost, high strength composites using cellulose fiber and engineering thermoplastics like nylon 6 and nylon 66. The primary difficulty here is the thermal degradation of cellulose fiber at high processing temperature.

1.2 References:

(1) James Morton, John Quarmley, and Lou Rossi, *the seventh international conference on woodfiber-plastic composites,* 3-6, 2003

(2) C. Klason, J. Kubat and H.E.Stromvall, *Intern. J. Polymeric Mater.,* 10, 159-187 (1984)

CHAPTER 2

INTRODUCTION AND LITERATURE REVIEW

2.1 Processing of Nylon/Cellulose fiber composites

2.1.1 Early Studies

In 1984 Klason and his co-workers [1] used cellulose-based fillers to reinforce PA6. During extrusion, appreciable darkening occurred, and the discolouration became more serious with the increasing of filler content. Higher contents produced pyrolytic degradation, 20% was the maximum filler concentration. The results showed that the elastic modulus increased a little, from 2.2 GPa to 2.8Gpa, but strength and elongation all decreased.

Cellulose fibers were degraded severely at processing temperatures beyond 200°C. The authors concluded that for higher melting temperature thermoplastics like PA-6, 'cellulosic fibres do not produce any significant degree of reinforcement despite their obvious stiffness and strength potential.'[1].

In 1985 Zadorecki and Abbas [2] used Reaction Injection Molding (RIM) to make cellulose-reinforced nylon-6 block copolymers. In this process two liquid component systems were injected into a closed mold where polymerization takes place. The processing temperature of RIM was 130°C so the degradation of cellulose was avoided, and since the RIM processing was carried out at low pressure levels, the fiber length reduction was avoided. The maximum fiber contents were limited from 7% to 15%, according to the cellulose fiber types. The flexural modulus of nylon copolymer

composite with 10% cellulose fiber was 2.16GPa, and impact strength was 8.0KJ/m^2. This processing can't get composites with high fiber contents because the viscosity increases rapidly with the increase of fiber content.

2.1.2 **Low temperature compounding**

Even though the early research didn't give encouraging result, the automotive and construction market needs for a low density reinforcement for engineering thermoplastics inspired researchers to take a second look at the wood fiber reinforced engineering thermoplastics.

In recent years, USDA Forest Products Lab and Rayonier Inc. cooperated to develop a unique compounding method called 'low temperature compounding (LTC)' to produce cellulose pulp fiber/PA-6 composites [3-6]. This method has three phases: start up conditions, a transition phase, and steady-state conditions. In the start up conditions, the temperature zones of extruder are set at 232ºC, a little bit higher than the melt temperature of PA6. With the addition of cellulose fiber, the melt viscosity will increase. The increase of melt viscosity will cause the melt temperature and torque load on the extruder to increase dramatically, which will lead to the degradation of cellulose fiber. So, the temperature of zones 4-7 is gradually reduced. This process is called 'transition phase'. At steady-state conditions, the twin screw extruder is at equilibrium. The temperature zones 1-3 are set at 232 ºC, while zones 4-7 are set at 149 ºC. The shear heating in the twin screw maintains the composite melt.

During processing, careful attention is needed. If there's any interruption in the flow of either PA6 or cellulose pellets during steady state conditions, material freezing in the extruder will happen, and a torque overload will end the compounding sequence.

The extruded composite pellets then were injection molded to ASTM test specimens. This processing is called low temperature injection molding (LTIM) because the nozzle temperature was held at 227 ºC, and the temperature along the three heat zones of the screw was held at 232 ºC, just above the melting temperature of nylon 6. The mechanical properties of PA-6 composites are shown below, where HPK means hardwood prehydrolyzed kraft (HPK) fiber with 98% alpha-cellulose, and SPS means softwood prehydrolyzed sulfite (SPS) fiber with 98% alpha-cellulose.

Table 2.1 Mechanical properties of PP and PA-6 composite [5]

	Tensile strength	Flexural strength	Tensile modulus	Flexural modulus	Notched Izod	Unnotched Izod
	(MPa)		(GPa)		(J/m)	
Polypropylene	27.6	28.7	1.39	1.39	16.1	556.4
PP + 33% wood flour	33.1	49.3	3.38	3.19	18.7	75.4
Nylon 6 (PA-6)	60.2	64.2	2.75	2.38	24	746.3
PA-6 + 30% wollastonite	62.7	105.7	6.51	6.27	25.8	173.9
PA-6 + 33% glass fiber	111.2	146.7	8.02	7.55	45.9	406.1
PA-6 + 33% HPK fiber	86.5	121.6	5.71	5.88	25.3	318.3
PA-6 + 33% SPS fiber	81.9	113.9	5.35	5.45	25.1	247.2

Using the same idea, the researchers also made PA-6,6/ cellulose fiber composites. 2% of plasticizing processing aid was used to lower the melting temperature of PA-6,6 since the melting temperature of PA-6,6 is 255 ºC. The tensile modulus is given on Figure 2.1 [5].

Even though low temperature injection molding was used, degradation is observed during injection molding. In 2003, Herman Winata, et.al [3] used microcellular injection molding (MuCell) to get cellulose fiber reinforced PA6 composite samples from the cellulose fiber/PA6 pellets. Mucell is to blend supercritical fluids with polymer melt to

creat a single phased polymer-gas solution. One of the advantages of this processing is the reduction of the material viscosity and processing temperature.

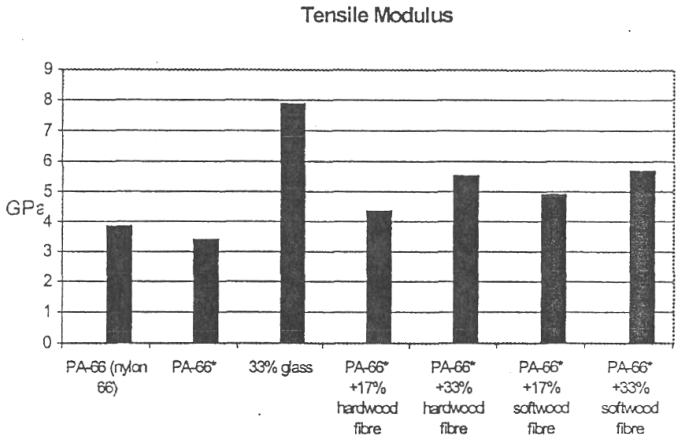

Figure 2.1 Tensile modulus of PA-66 composites. PA-66* contains 2% plasticizer [6]

Compared with conventional injection molding, the temperature of the middle zones used in microcellular injection molding is reduced from 210ºC to 187ºC in order to reduce the thermal degradation of the reinforcing cellulose fibers. The sample color of conventional injection molding became dark brown, while its microcellular sample exhibits a light brown color. This may suggest reduced degradation. However, presence the microcells can also contribute to the lightening of the color. Figure 2.2 and 2.3 show the tensile strength and tensile modulus of conventional injection molding and microcellular injection molding. The tensile properties of the microcellular injection molded samples decrease compared with their conventional solid counterparts.

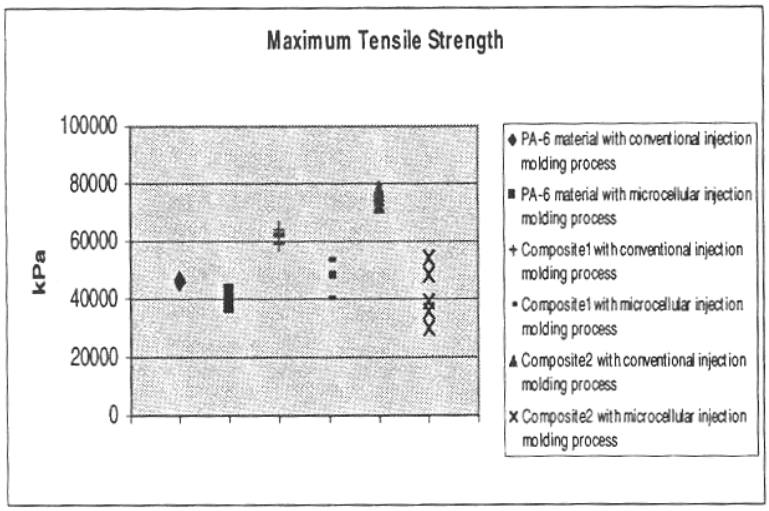

Figure 2.2 Maximum tensile strength for solid and microcellular PA-6, PA-6/cellulose fiber composite, and PA-6/cellulose fiber wollastonite composite.[3]

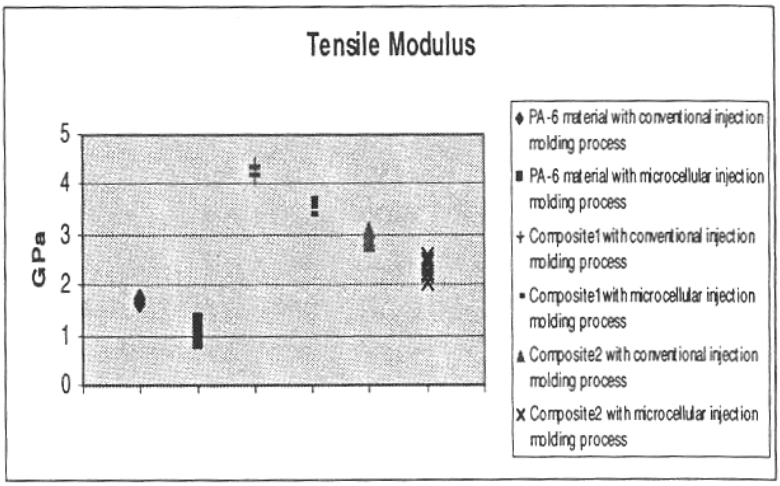

Figure 2.3 Maximum tensile modulus for solid and microcellular PA-6, PA-6/cellulose fiber composite, and PA-6/cellulose fiber wollastonite composite.[3]

SEM micrographs (Figure 2.4 and 2.5) show that microcellular injection molding method introduces microcells with the sizes ranging from 1 to 60μm. Cell nucleation tends to take place at the interface between the polymer and the additives. These voids

may offset the fiber reinforcing functions significantly. This is why in the mechanical tests microcellular injection molded composites tend to have lower strengths.

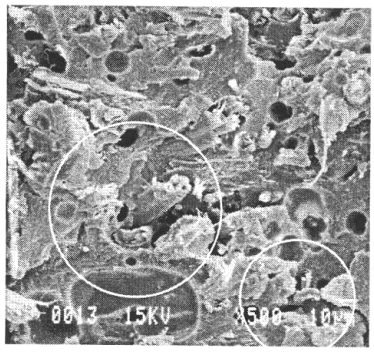

Figure 2.4 SEM of Microcellular injection molded PA-6/cellulose fibers [3]

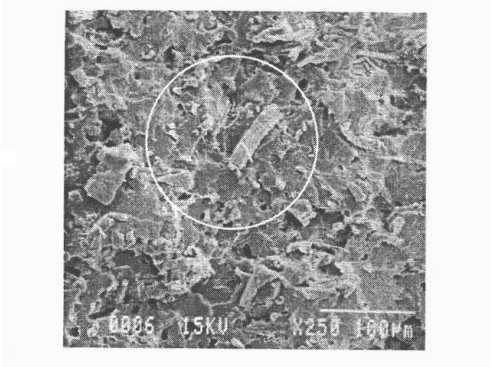

Figure 2.5 SEM of Conventional injection molded PA-6/cellulose fibers [3]

2.1.3 Michigan State University, Lowering the Melting Temperature of Nylon

In 2003, Misra, et al [7] used small quantities of inorganic salts during melt extrusion processing to depress the melting temperature of nylon 6. They added Lithium chloride (LiCl) salt into nylon 6 during extrusion. Then the nylon 6 and salt mixture were used as matrix and hemp natural fibers were incorporated into the matrix using the extrusion compounding technique. Composite pellets were injection molded into test specimens.

Table 2.2 shows the melting temperature of nylon 6/LiCl mixture. And Table 2.3 shows the heat deflection temperatures of the nylon 6 plastics and the composites. 3% LiCl in nylon is chosen to keep the concentration of LiCl at a low level. Figure 2.6 shows the tensile properties of nylon 6 plastics and composites. The addition of LiCl to nylon 6 decreases the crystallization temperature and degree of crystallinity. The heat deflection temperature of nylon 6 decreased to 44ºC from 154ºC of neat nylon 6. With the addition of natural fiber the HDT increases to as high as 184ºC. Both tensile modulus and strength increase by 275% and 30% with the reinforcement of modified nylon 6 with 40% hemp fiber.

Table 2.2 Melting Temperatures of Various Compositions as measured by DSC [7]

Composition	Melting Temperature (C)
Neat Nylon 6	223
Nylon 6 + 2.5wt%LiCl	209
Nylon 6 + 3.0wt%LiCl	199
Nylon 6 + 3.5wt%LiCl	194
Nylon 6 + 5.0wt%LiCl	191

Table 2.3 Heat Deflection Temperatures of the Nylon 6 Plastics and the Composites [7]

Composition	Heat Deflection Temperature (C)
Neat Nylon 6	154
Modified Nylon6	44
Modified Nylon6 + 30 wt% Hemp Fiber	164
Modified Nylon6 + 40 wt% Hemp Fiber	184
Nylon 6 + 30 wt% Glass Fiber	> 220

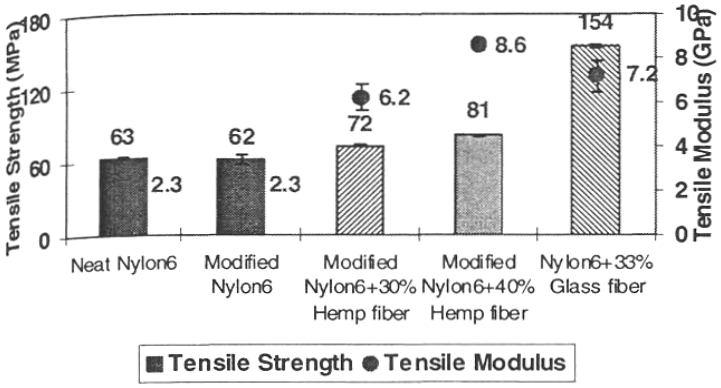

Figure 2.6 Comparison of Tensile Properties [7]

2.2 Fiber/matrix interface

Fiber/matrix interface is an important parameter to affect the processing and final properties of composites. There's a lot of research focused on how to improve the interfacial adhesion between polypropylene and natural/wood fiber because of the incompatibility between PP and wood fiber. Since there're few reports about cellulose fiber/nylon 6 or nylon 66 composites, there isn't much information about the composite interface. From the chemical structures of polyamide and cellulose fiber, both of them have hydrogen bond, which make better compatibility between cellulose fiber and polyamide.

E. McHenry and Z. H. Stachurski [11] studied the interface between nylon-wood fiber and polypropylene-wood fiber composite materials without any additives. The fiber was eucalypt hardwood fiber, matrix materials were nylon fiber obtained from stockings, and polypropylene pellets. A hot press technique was used to manufacture the composite. Fracture surfaces were examined using SEM. No fiber pullout was observed for nylon/wood fiber composite (Figure 2.7), and fiber pullout was observed for PP based

composite material (Figure 2.8). The authors claimed that this indicated efficient bonding occurred between the wood fibre and Nylon.

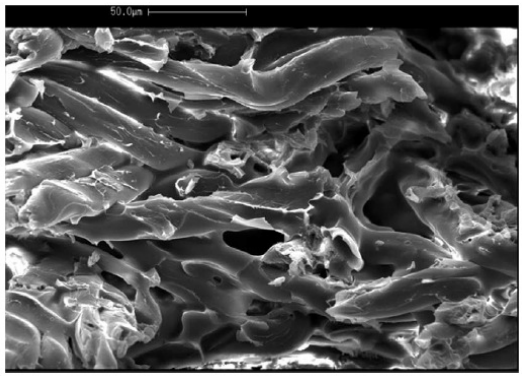

Figure 2.7 SEM mircograph of Nylon-wood fibre composite fracture surface showing partially melted nylon fibre [11]

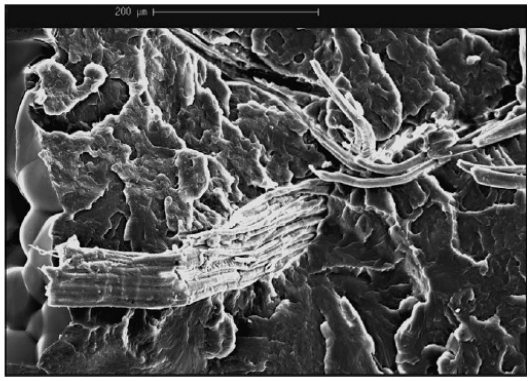

Figure 2.8 SEM micrograph of PP composite fracture surface showing fibre pull out and poor interfacial adhesion [11]

In 1994 M. Garcia-Remirez, et al [14,15], made cellulose-polyamide 66 blends by mixing solutions of PA66 and cellulose. N-methyl morpholine N-oxide and phenol (80/20w/w) was used as solvent. After spinning or casting, fibers or films were precipitated in methanol. PA 66 forms semicrystalline domains embedded in an amorphous cellulose matrix (PA 66 0-70%). This composite is different with the composites introduced before, but the interface of these two composites may be comparable. A model which involves perfect adhesion between domains was used to

predict the mechanical behavior. The experimental and predicted data fit very well, which means that there is a strong adhesion at their interface. Solid state ^{13}C nuclear magnetic resonance has also been used to study these samples and supports the existence of strong interactions between both PA66 and cellulose.

UCSD Forest Product Lab and Rayonier Inc. [12] studied the effect of titanate compatibilizer (L44-N) on flexural properties of nylon 6/cellulose fiber composites. The presence of L-44-N enhanced performance of all the composites.

Chen, Huang and Zhan [13] used a coupling agent with carboxyl to enhance the adhesion between thermomechanical wood pulp and nylon 6 . The mechanical properties of composites with and without coupling agent are shown in Figure 2.9. Without coupling agent, the properties of composite is lower than neat polymer, and with coupling agent, properties increase with fiber content.

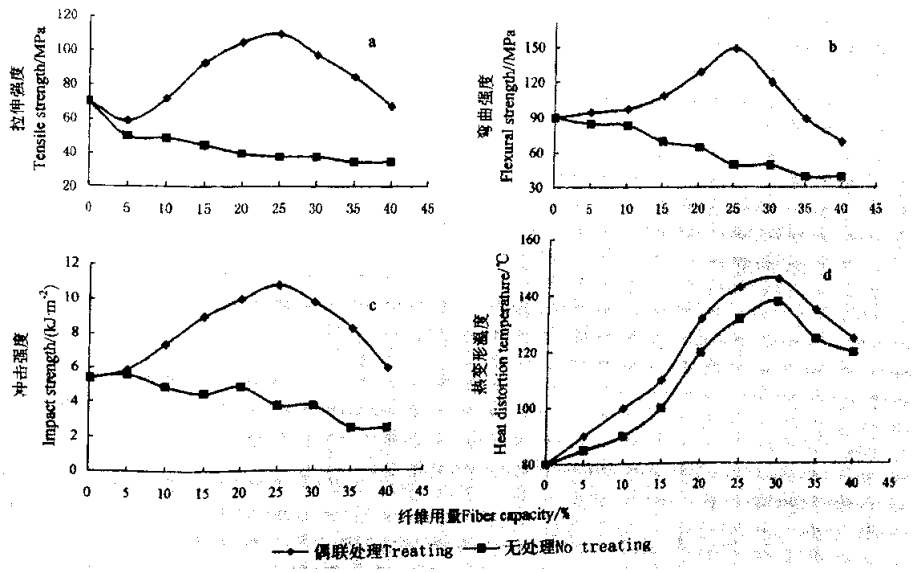

Figure 2.9 Effect of coupling agent on composite properties [13]

There's not much literature available about nylon/cellulose fiber composites, and there's no systematic research on this composite. From the literature review above, the following conclusions can be drawn:

- It's not easy to get high melting temperature polymer/natural fiber composite by conventional extrusion/injection molding processing because natural fiber will degrade at high temperature.
- Two methods were used to get nylon/cellulose fiber composites. One is to lower the melting temperature of nylon by adding inorganic salts; another is to lower the processing temperature and let the shear heating maintain the composite melt.
- Unlike PP/natural fiber composites, nylon/cellulose fiber have strong interactions because both of them have hydrogen bonds.
- Compatibilizers/coupling agents may increase mechanical properties of the composites.

2.3 Effects of processing parameters on properties of composites

The mechanical properties of the composites are strongly influenced by a number of factors such as fiber length, fiber dispersion, fiber degradation, and fiber orientation. The processing parameters, such as screw speed, feeding rate and temperature profiles, will affect the final properties of composites by influencing these factors. A lot of studies about the effects of processing characteristics on mechanical properties of glass fiber reinforced thermoplastics have been reported [21-25].

Ulku Yilmazer and Murat Cansever [23] studied the effects of processing conditions on the fiber length distribution of glass fiber reinforced nylon 6. They concluded that

fiber length was mainly determined by shear rate and gave the major factors that affect the shear rate: $\dot{\gamma} \propto \frac{SS * f}{FR}$

Where $\dot{\gamma}$ is the average shear rate, *SS* is the screw speed, *f* is the fill ratio and *FR* is the total feed rate. The last three variables are also related.

This relationship was evaluated using nylon 6 / 30% glass fiber composites. The composites were extruded with a co-rotating twin screw extruder. Screw speeds were chosen to be 250rpm, 300rpm, and 350rpm. Feed rates were 70, 80, and 90kg/hr. Effects of different processing factors on fiber length distribution were studied. We can see from Table 2.4 and Figure 2.10 that for all cases the fiber length decreases as the screw speed increases, as expected. The extent of fiber degradation for the increase in the screw speed from 250 to 300rpm is higher than that of 300 to 350rpm. At higher screw speed, temperature is increased because of the viscous heat generation. So at higher screw speeds, higher temperature and lower viscosity may result in a lower shear stress acting between the glass fiber and the polymer matrix at the interface, consequently the fiber length may decrease less than proportionally to the screw speed. Similarly, the feed rate will affect the fiber length, too. Screw speed, feed rate and feed ratio will all affect the fiber length.

Table 2.4 Dependence of the average fiber length and process properties on the screw speed and the feed rate [23]

FR (kg/h)	SS (rpm)	xL_w	xL_n	nL_w	nL_n	W_f	T_m (°C)	Pm (bar)	Trq (%)
70	250	478	195	291	141	29.0	259	18	71
70	300	438	162	279	104	29.4	260	16	63
70	350	434	155	266	146	29.0	261	15	60
80	250	437	128	302	134	29.0	257	20	80
80	300	413	145	271	119	29.1	259	18	70
80	350	406	122	278	120	29.0	260	16	65
90	300	496	179	291	114	29.0	256	20	78
90	350	432	152	278	115	29.1	259	18	71

FR = Feed Rate, SS = Screw Speed, xL_w = Weight Average Fiber Length Following Extrusion, xL_n = Number Average Fiber Length Following Extrusion, nL_w = Weight Average Fiber Length Following Injection Molding, nL_n = Number Average Fiber Length Following Injection Molding, W_f = Weight Fraction of Fibers, T_m = Melt Temperature, P_m = Melt Pressure, Trq = Torque.

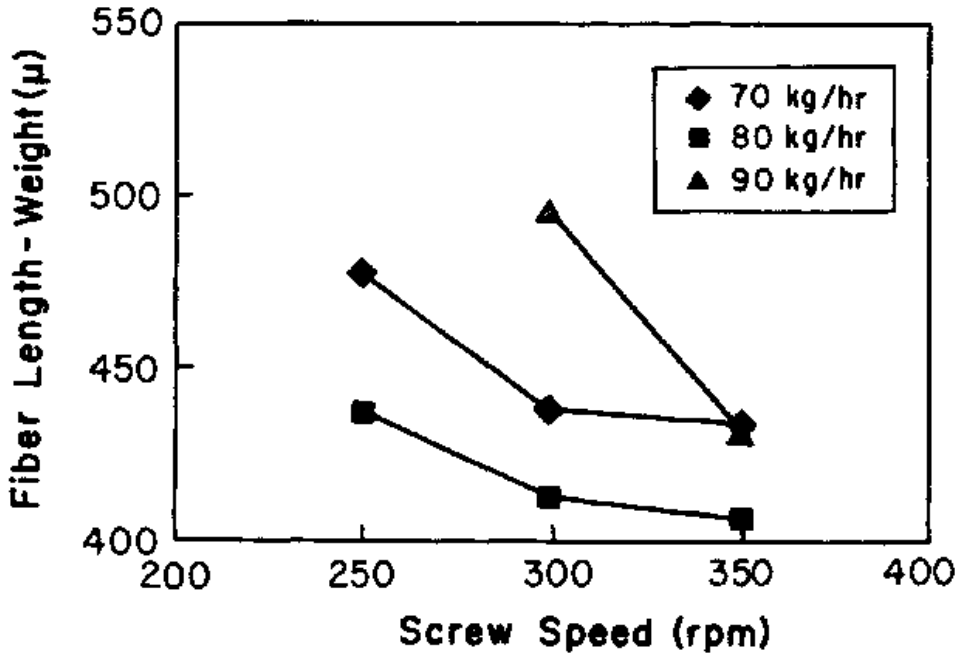

Figure 2.10 Dependence of the weight average fiber length on the screw speed [23]

Cellulose fiber is a little different with glass fiber because cellulose fiber is more flexible. Czarnecki, et al [26] compared the rheological behavior and fiber damage of glass and cellulose fiber reinforced polystyrene melts. They found that glass fibers break down rapidly to very small aspect ratios while cellulose fibers showed less damage than glass fibers. They also mentioned that the viscosity of the melt materials increases with fiber percentage increase.

Temperature profiles and mixing time are important factors for natural/wood fiber reinforced composites because the thermal degradation of natural/wood fiber. For natural/wood fiber reinforced composites, sometimes these two factors are dominant and need to be considered first during study [27-29].

Stade [21] studied the temperature profile in a extruder. He introduced the kneading teeth with thermocouples arranged around the screw to measure the actual temperature of

melting mixture. He found that introducing the glass fibers to the polymer melt initially reduces the melt temperature, but subsequently, leads to a rapid rise in temperature due to the increased viscosity of the compound. See Figure 2.11.

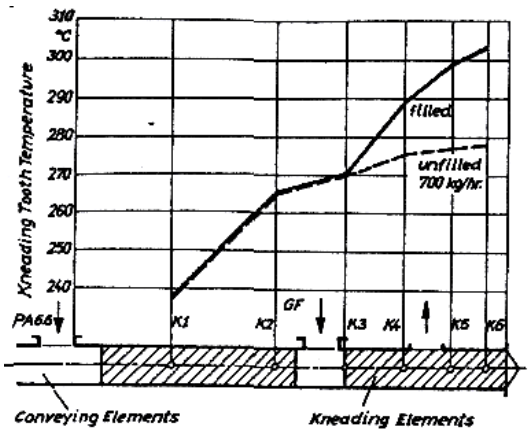

Figure 2.11 Temperature profile in a two-stage continuous mixer for the processing of filled and unfilled PA 6, 6 with 30% glass fiber [21]

P.V. Joseph, etc [27] studied the effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites. PP/sisal was mixed in a Haake Rheocord Mixer, the mixture was subjected to sheeting in a two roll mill while it's still hot. Figure 2.12 shows the effect of mixing time. When mixing time is too short, tensile strength and Young's modulus are low because of the ineffective mixing and poor dispersion of the fiber in PP matrix. As the mixing time increases fiber dispersion becomes better and properties are improved. However, as the mixing time increases, fiber breakage becomes predominant so properties decrease. Figure 2.13 shows the effect of mixing temperature. With constant rotor speed and mixing time, tensile strength of the composites increases with the rise in temperature and then decreases, showing maximum improvement at 170 ºC. At low temperature the viscosity of the mixture is very high, and this causes the break down of the fibers during mixing. The decrease of strength at a

mixing temperature above 170 ºC can be due to the thermal degradation of the wood fibers. Moreover the dispersion of fiber in PP will be poor due to the decrease in viscosity at high temperature. For the effect of mixing speed, Figure 2.14 shows that tensile strength increases with the rise in rotor speed up to 50rpm and then decreases. At low rotor speed, the poor dispersion of fiber in PP causes the low tensile strength and at too high rotor speed, fiber breakage is dominant and causes reduction in strength. Takase and Shiraishi give the same trends using wood/PP composite [28].

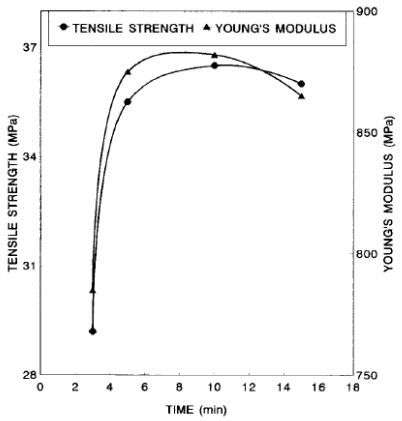

Fig. 2.12 Variation of tensile strength and modulus with mixing time of melt-mixed composites [27]

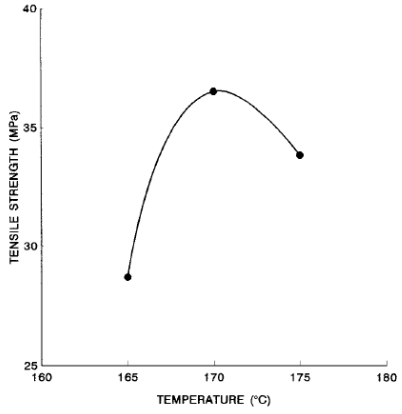

Figure 2.13 Variation of tensile strength with temperature of melt-mixed composites [27]

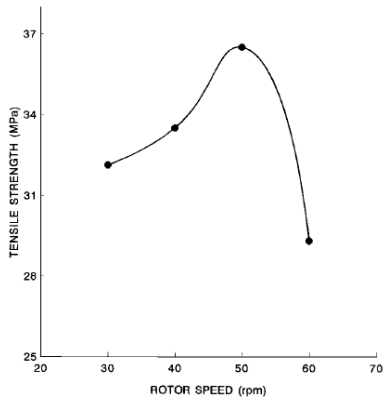

Fig. 2.14 Variation of tensile strength with rotor speed of melt-mixed composites [27]

With the above review we can see that many process parameters, such as screw speed, feeding rate, temperature profiles, melting time, etc, will affect the mechanical properties of composites. To optimize processing, we need to consider many parameters and their interactions.

2.4 Proposed work

1. Processing

The continuous extrusion - direct compression molding processing will be chosen to make cellulose fiber/nylon 6 or 66 composites. Matrices and cellulose fiber will be mixed by a twin screw extruder. The hot mixture will be collected and compression molded directly to desired products while the polymer is still melted. Unlike the conventional extrusion/injection molding process, this method shortens the thermal history of cellulose fiber by avoiding the re-melting during injection molding, thus the thermal degradation of cellulose fiber is decreased. And this is a low cost route to get molded products.

Extrusion-injection molding processing will be used to compare with the extrusion-compression molding process. Extruded composite will be milled and injection molded to test samples. The effect of a second heat history on fiber length degradation caused by injection molding will be studied.

2. Mechanical properties tests

The extrusion-compression procedure will provide 12”x12” or 8”x8” square plaques. The plaques will be cut into 1”x5” rectangle for flexural test, dog bone shape for tensile test, and 0.5”x 2.5” square for Izod impact test. Extrusion-injection molding procedure will produce test samples directly. Tensile, flexural and Izod impact tests will be performed according to ASTM D 638, ASTM D 790 and ASTM D 256, respectively.

3. Effect of processing parameters

Many processing parameters will affect the properties of final products. For extrusion, temperature profiles will effect the fiber degradation. Also, screw speed and feeding rate will change fiber length and orientation. For compression molding, the temperature of the mold and cooling speed will change the crystalline morphology of matrices. Mechanical properties are the reflection of all these changes. The processing parameters will be optimized to get best properties.

4. Prediction of mechanical properties of composites

The matrix will be dissolved in formic acid while fiber will be left. The actual fiber content will be calculated. Fiber length distribution will be tested by Fiber Quality Analyzer (FQA). Effect of thermal treatment on the fiber properties will be evaluated. With the properties of matrix, fiber and fiber length distribution, we can set up theoretical models to predict the mechanical properties of the composite.

5. Cellulose fiber / recycled polymer

Most carpet manufactured in U.S.A consists of nylon 6 or nylon 66 face fiber, it is a good resource of engineering thermoplastics. The usage of recycled nylon 6 or nylon 66 as matrices can lower the cost of final products. After we optimize the processing of the nylon 6 or 66/ cellulose fiber composites, we can use the optimized conditions to get recycled nylon 6 or 66/cellulose fiber or wood fiber composites.

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CHAPTER 3

EXPERIMENTS AND DISCUSSION

3.1 Materials and Equipment

Table 3.1 & 3.2 show the materials and equipment used in experiments, including suppliers and types of materials, manufacturers and models of instruments.

Table 3.1 Materials Used in Experiments

Materials	Supplier	Comments
Cellulose fiber	CreaFill Fibers Corp.	TC 2500
Nylon 6	BASF® Corp.	Ultramid® B27 Spin Grade
Nylon 66	Solutia Inc.	
Polyurethane	Hydrosize® Technologies, Inc.	Hydrosize® U1-01
Formic Acid	Mallinckrodt Chemicals	88%
INTEC	International Technical Polymer Systems, Inc.	SB 94
Lithium Chloride	FMC Lithium Division	LiCl
N-Butylbenzenesulfonamide	Sigma-Aldrich. Inc	99% NBBSA
Thiourea	Sigma-Aldrich. Inc	99%
ε-Caprolactam	Sigma-Aldrich. Inc	99%

Table 3.2 Instruments Used in Experiments

Instruments	Manufacturer	Model
Twin Screw Extruder	NFM Welding Engineers, Inc.	HTR 30mm
Injection Molding Machine	Sumitomo Heavy Industries, Inc.	SG75
Compression Molding Machine	Georgia Composites	
Compression Molding Machine	Wabash	
Feeder I	AccuRate Inc.	
Feeder II	AccuRate Inc.	
Fiber Quality Analyzer (FQA)	OpTest Equipment Inc.	
SEM	Hitachi, Ltd.	S-800
TGA	Seiko	TG/DTA 320
DSC	TA Instruments	DSC 2920
Grinder	IMC Company	SK-15
TensilKut	Sieburg Industries, Inc.	10-76
Testing Machine	Instron Corp	4466
Brabender	C.W.Brabender Instruments, Inc.	
Izod Impact Machine	Custom Scientific Instruments, Inc.	
Capillary Rhometer	Dynisco Polymer Test	LCR 7000 Series

3.2 Experiments

3.2.1 Processing

One kind of cellulose fiber, TC 2500, is used as the reinforced fiber. TC 2500 is the longest fiber among the cellulose fibers provided by CreaFill Fibers Corp, it is expected to provide composites with the best properties. Nylon 6 or nylon 66 is the matrix. Fiber and polymer pellets are dried in oven at 120°C for at least four hours. The matrix and cellulose fiber will be mixed using a twin screw extruder. Figure 3.1 is a schematic figure of the twin screw extruder. It includes six separately heated zones and a die. Nylon 6 or 66 is added at the first zone feed throat. Cellulose fiber is introduced in zone 4, in the middle between the feed throat and die-face. Screw speed is 200 rpm for both nylon 6 and nylon 66 matrix composites. The production rate is chosen to be 12kg/hr, the fill ratio is 66%. Polymer pellets and fiber will be fed by ratio. For example, for 10% composites, feeding rate for pellets is 10.8 kg/hr, and for cellulose fiber is 1.2kg/hr. The temperature profiles of the extruder for nylon 6 and nylon 66 composites are shown in Table 3.3 and Table 3.4.

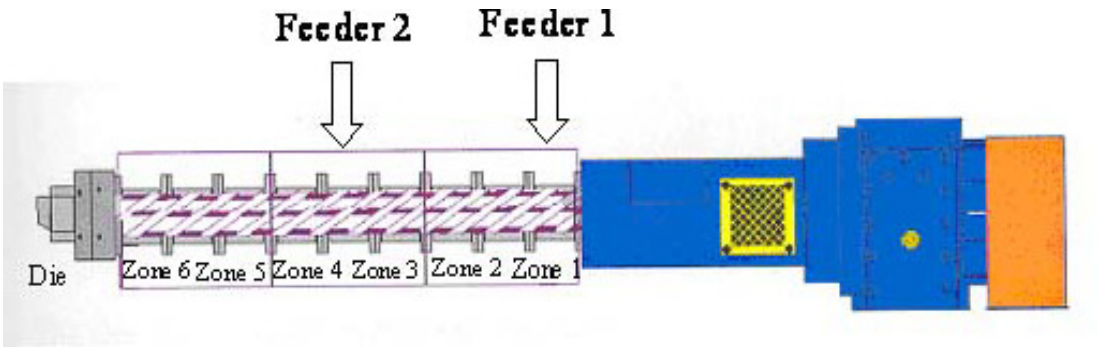


Figure 3.1 Schematic figure for twin screw extruder[1]

Table 3.3 Extrusion temperature profile for nylon 6/cellulose fiber

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
210	220	230	235	240	230	200

Table 3.4 Extrusion temperature profile for nylon 66/cellulose fiber

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
250	260	265	270	270	270	240

The hot mixture from the die is collected for one minute and compression molded directly to a plaque while the polymer is still melted. During compression molding, 1/8" thick sheet is put between the top and bottom molds to control the plaque thickness. The plaque will be cut to samples for flexural, tensile, and Izod impact testing.

Extrusion-injection molding processing will be used to compare with the extrusion-compression molding process. Composites coming from extruder will be ground to small pieces by the IMC grinder and injection molded into test samples. The injection molding processing conditions for nylon 6 and nylon 66 composite are shown on Table 3.5 and 3.6. Zone 4 shown on the screen of the injection molding machine is actually covered by zone 3 and zone 5, which means that zone 4 doesn't exist. We don't need to set the temperature of zone 4.

Table 3.5 Injection molding temperature profile for nylon 6/cellulose fiber

Temperature (^{o}C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
230	230	230	210	205	38	35

Table 3.6 Injection molding temperature profile for nylon 66/cellulose fiber

Temperature (^{o}C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
265	265	265	250	240	49	35

3.2.2 Mechanical Testing

Tensile test samples were prepared according to ASTM D638, type 1. The injection molded samples were molded directly to the dog bone shape. The compression molded plaque was first cut to 6.5"x 0.75" rectangular bar then milled to dog bone shape by a Tensikut mill machine. All the tensile tests were conducted at room temperature with an Instron 4466 universal test machine. The crosshead speed war 0.2 in/min. The detailed procedure in ASTM D638 was followed.

Flexural testing is performed according to ASTM D 790. The injection molded samples were molded to 1/2" x 5" rectangular samples. The compression molded plaque was cut into 1" x 5" rectangular samples. The samples were tested at room temperature on an Instron 4466 machine. The span length between two supporting noses was 2" and crosshead speed was 0.533 in/min. .

Izod impact tests will be performed according to ASTM D 256. The samples were cut to 1/2'' x 2 1/2'' rectangular bars. The rectangular bars were notched on one side, the depth of the composite material remaining in the specimen under the notch was 0.4''.

3.2.3 Fiber content/length analysis

The tested samples were cut to small pieces and were put into formic acid for three days. Nylon 6 or nylon 66 was dissolved by formic acid and cellulose fiber was left. The cellulose fiber was filtered and washed by formic acid, then dried in vacuum oven for four hours. By measuring the weight of composite and fiber we can calculate the actual fiber content.

Cellulose fiber length was measured by Fiber Quality Analyzer (FQA). Fiber was diluted with D.I. water. Diluted fiber enters a thin planar channel. This channel helps to gently orient the fiber 2-dimensionally, so that the fiber is fully viewed by the camera. The picture taken by the camera is then analyzed by the software to give the fiber length, curl, etc.

3.2.4 Morphology Analysis

The Izod impact samples were ruptured by the test machine and the fracture surfaces were examined. Also the Izod impact samples were cooled in liquid nitrogen for 4 hours and broken while it's cold. The surface was etched with formic acid for 1 day. Nylon 6 or nylon 66 dissolved and cellulose fiber was exposed. All the surfaces were coated with gold. A Hitachi S-800 Scanning Electron Microscope (SEM) was used to study the fracture surface and dissolved surface of nylon 6 or 66/cellulose fiber composites.

3.2.5 Density Measurement

The density of composites was determined by ASTM D792. The samples were weighed both in air and water and the density was calculated by

$$\rho = a/((a-w)\rho_{water})$$

Where ρ is the sample density in g/cm^3, a is the weight in air in g, w is the weight in water in g, and ρ_{water} is the density of the water in g/cm^3.

3.2.6 DSC

The Differential Scanning Calorimetry (DSC) was used to determine the melting temperature and solidification temperature of matrix. For nylon 6, the material was first heated from 30^o C to 260^o C, then cooled from 260^o C to 30^o C. For nylon 66, the heating range was from 30 to 300^o C. The temperature ramp was set to be 10^o C/min.

3.2.7 TGA

Thermogravimetric Analysis (TGA) was used to determine the thermal degradation of cellulose fiber with increasing of temperature. Cellulose/wood fiber was heated to 500 ^{o} C with the heating rate of 10^o C.

3.2.8 Rheology

The Dynisco polymer test LCR 7000 series capillary rheometer was used to test the viscosity vs. shear rate of matrix or composite. For nylon 6 matrix composites, the temperature was 230^o C. For nylon 66 matrix composites, the temperature was 270^o C. The length of the die is 40mm. The diameter of the die is 1mm. Since we didn't calibrate the effect of die, the viscosity vs. shear rate is actually apparent viscosity vs. apparent shear rate.

3.3 Results and Discussion

3.3.1 Characterization of cellulose fiber

CreaFill Fibers Corp. provided two kinds of cellulose fiber, TC 2500 and TC 150. According to the data given by the company, the average length of TC 150 and TC 2500 is 120μm, and 900μm, respectively. The average width of these two fibers is both 20μm. Wood fiber (Kraft pulp) is provided by IPST.

Thermogravimetric analysis (TGA) of these three kinds of fibers is shown in Figure 3.2. The thermal degradation temperature of cellulose fiber is higher than wood fiber. This high degradation temperature (280°C) should allow cellulose fiber to reinforce high melting temperature plastics such as nylon 6 and nylon 66. To see if the fiber degrades faster in air, TGA was done in both nitrogen and air environment. The result shows that oxygen doesn't accelerate the degradation of fibers.

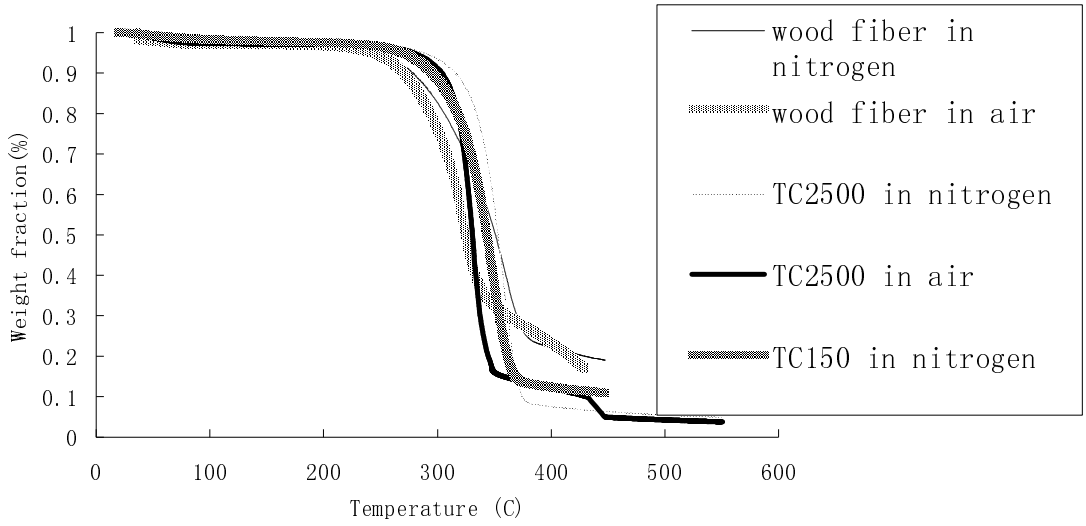


Figure 3.2 Thermogravimetry of cellulose and wood fiber

The fiber length distribution is measured by a Fiber Quality Analyzer (FQA). The fiber length measured by FQA is much lower than the numbers provided by company. Especially for TC 2500, the fiber length we measured is 0.283mm, much shorter than 0.9mm.

Table 3.7 Fiber length of cellulose fiber and wood fiber

Fiber	Mean Length (measured)		Mean Arithmetic Length provided by company (mm)
	Arithmetic (mm)	Length weighted (mm)	
TC 150	0.128	0.147	0.120
TC 2500	0.283	0.506	0.900
Wood fiber	0.211	0.517	

3.3.2 Color change of samples with different fiber contents and processing procedures

Figure 3.3 shows the color changes with different fiber contents and procedures. With the increase of fiber content, the color of the composite becomes darker. Nylon 66/cellulose fiber composite is darker than the nylon 6/cellulose fiber composite at the same fiber content. Extrusion-injection molding processing leads to darker samples than the extrusion-compression molding process. The darker color implies more severe thermal degradation of the cellulose fiber during processing.

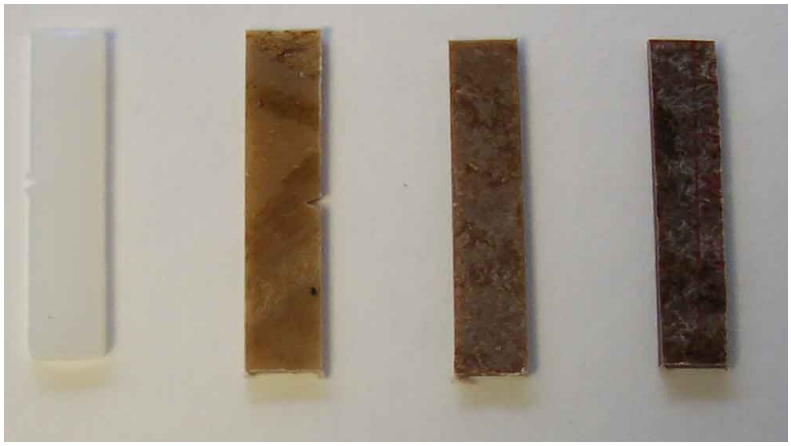


Figure 3.3a Nylon6/cellulose fiber by extrusion-compression molding (0%, 10%, 20%, 30% cellulose fiber from left to right)

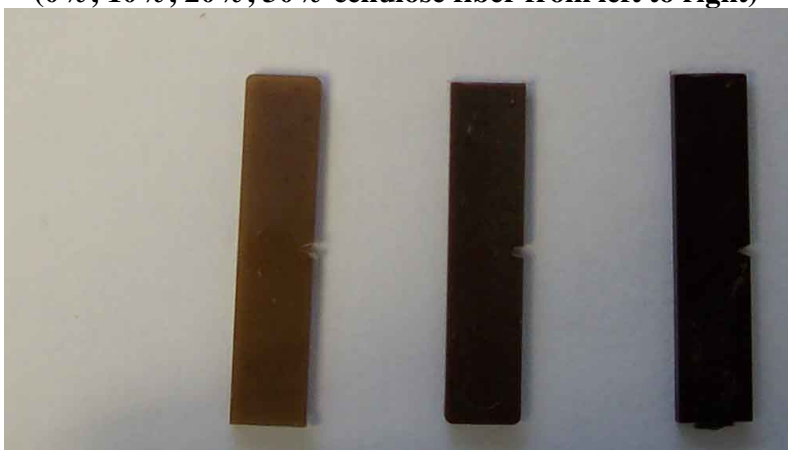


Figure 3.3b Nylon6/cellulose fiber by extrusion-injection molding (10%, 20%, 30% cellulose fiber from left to right)

Figure 3.3c Nylon66/cellulose fiber by extrusion-compression molding (0%, 10%, 20%, 30% cellulose fiber from left to right)

3.3.3 Densities and Mechanical Properties

3.3.3.1 Actual Fiber Contents and Densities

The fiber contents of composites were controlled by the feeding rate of matrix and fiber. However, the feeding rate can't be calibrated precisely, especially the feeding rate of cellulose fiber. Table 3.8 shows the densities and actual fiber contents of composites with different components and different procedures.

Comparing the densities of nylon 6/cellulose fiber composites made by the two procedures, we can see that the composites made by extrusion-injection molding have higher density than composites made by extrusion-compression molding at the same fiber content. 20% cellulose fiber/nylon 6 made from extrusion-compression molding has a higher density because its actual fiber content is 3% higher than the composite made by extrusion-injection molding. The different densities show that injection molding gives samples with less voids than compression molding.

The nylon 66/cellulose fiber composites have lower densities than nylon 6/cellulose fiber composites at the same fiber content even though nylon 66 has a slightly higher density than nylon 6. This can be explained by the processing conditions. To decrease fiber degradation, the processing temperature is set just above the melting temperature of nylon 66. When we collect the hot mixture from extruder, the mixture starts to solidify before the compression molding. The early solidification of composites may cause more voids. The extrusion-compression molding and extrusion-injection molding used the same samples from extrusion. They should have the same actual fiber content. But the measurement shows that fiber content of injection molding is slightly lower than the

compression molding, which means injection molding caused more thermal degradation of fiber.

Table 3.8 Densities and actual fiber contents

	Density (g/cm^3)	Actual Fiber Content
Nylon 6/Cellulose Fiber Composites		
Extrusion -Compression Molding		
N6/10%CF	1.150	14.8%
N6/20%CF	1.209	28.4%
N6/30%CF	1.237	34.2%
Injection Molding		
Nylon 6	1.131	0
Extrusion –Injection Molding		
N6/10%CF	1.160	13.3%
N6/20%CF	1.196	25.0%
N6/30%CF	1.247	33.3%
Nylon 66/Cellulose Fiber Composites		
Injection Molding		
Nylon 6,6	1.145	0
Extrusion –Compression Molding		
N66/10%CF	1.158	9.8%
N66/20%CF	1.198	26.6%
N66/30%CF	1.229	34.1%

3.3.3.2 Tensile properties

Table 3.9 Tensile properties of nylon 6/cellulose fiber composites

Mean

	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Injection Molding			
Neat nylon 6	26.3	44.2	1.92
Extrusion -Compression Molding			
N6/10%CF (14.8%)	2.84	53.7	3.01
N6/20%CF (28.4%)	1.98	54.3	4.16
N6/30%CF (34.2%)	1.31	48.9	4.58
Extrusion –Injection Molding			
N6/10%CF (13.3%)	3.29	47.9	3.12
N6/20%CF (25.0%)	2.15	54.2	4.32
N6/30%CF (33.3%)	1.63	53.3	5.15

Standard Deviation

Injection Molding			
Neat nylon 6	3.04	0.39	0.118
Extrusion -Compression Molding			
N6/10%CF (14.8%)	0.196	2.21	0.272
N6/20%CF (28.4%)	0.451	4.87	0.772
N6/30%CF (34.2%)	0.287	3.88	0.947
Extrusion –Injection Molding			
N6/10%CF (13.3%)	0.099	2.07	0.180
N6/20%CF (25.0%)	0.416	1.47	0.696
N6/30%CF (33.3%)	0.232	2.69	0.331

The comparison of the tensile properties of nylon 6/cellulose fiber composites with different procedures and fiber contents is shown on Table 3.9. The strain of composites decreases with increasing fiber content. Modulus increases with increasing fiber content with both procedures. Compared with neat nylon 6, the composites have higher tensile stress. 20% cellulose fiber content gives highest stress for both procedures. But the stress of composites doesn't change a lot with the different fiber contents.

The mechanical properties are slightly different between extrusion-compression molding and extrusion-injection molding. Extrusion-compression molding processing decreases the thermal degradation of cellulose fiber, and has longer fiber length. Extrusion-injection molding processing gives better samples with less voids and flaws. There's a trade-off between these two processes. The extrusion-compression molding gives a little bit lower strain and modulus than extrusion-injection molding, but we can say that composites obtained from the two procedures have comparable properties.

3.3.3.3 Flexural properties

Table 3.10 and Table 3.11 show the flexural properties of nylon 6/cellulose fiber and nylon 66/cellulose fiber composites, respectively. From Table 3.10, we can see that for extrusion-compression molding, the stress of composites is a little bit lower than neat nylon 6 and with 30% fiber content, the stress is decreased significantly. With the increase of fiber content, the flexural strain decreases, modulus increases, but the composite with 30% fiber content has lower modulus than 20% fiber content. For the extrusion-injection molding, the stress and modulus all increase, and strain decreases with the increase of fiber content.

Table 3.10 Flexural properties of nylon 6/cellulose fiber composites

Mean

	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion -Compression Molding			
N6/10%CF (14.8%)	6.21	103	2.72
N6/20%CF (28.4%)	3.00	103	3.69
N6/30%CF (34.2%)	2.80	93.3	3.52
Injection Molding			
Nylon 6	7.36	69.8	1.37
Extrusion –Injection Molding			
N6/10%CF (13.3%)	7.06	71.6	1.57
N6/20%CF (25.0%)	6.79	85.6	2.00
N6/30%CF (33.3%)	5.11	95.7	2.60

Standard Deviation

Extrusion -Compression Molding			
N6/10%CF (14.8%)	0.599	6.21	0.235
N6/20%CF (28.4%)	0.306	10.9	0.167
N6/30%CF (34.2%)	0.234	7.93	0.161
Injection Molding			
Nylon 6	0.152	1.03	0.018
Extrusion –Injection Molding			
N6/10%CF (13.3%)	0.233	0.63	0.0227
N6/20%CF (25.0%)	0.220	1.07	0.0386
N6/30%CF (33.3%)	0.687	3.03	0.0706

The properties of nylon 66/cellulose fiber composites have the same trends as the nylon 6/cellulose fiber composites. With the increase of fiber content, the modulus increases, strain decreases and the failure stress is lower than the neat nylon 66.

Table 3.11 Flexural properties of nylon 66/cellulose fiber composites

Mean

	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion -Compression Molding			
Nylon 66	3.70	74.7	2.32
N66/10%CF (9.8%)	2.19	63.1	2.92
N66/20%CF (26.6%)	1.98	62.5	3.35
N66/30%CF (34.1%)	2.07	69	3.58

Standard Deviation

Extrusion -Compression Molding			
Nylon 66	1.77	24.6	0.231
N66/10%CF (9.8%)	0.535	19.2	0.321
N66/20%CF (26.6%)	0.301	13.6	0.745
N66/30%CF (34.1%)	0.336	9.5	0.200

The extrusion-compression molding used the 1’ wide samples while extrusion-injection molding get 1/2’ wide samples so the properties are not comparable. Table 3.12 shows the difference between 1’’ and 1/2’’ flexural samples. The 1’’ and 1/2’’ samples are cut from the same compression molded plaque. The stress and modulus of 1’’ samples are a little bit higher than 1/2’’ samples.

Table 3.12 Difference between 1'' and 1/2'' flexural samples

	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
1'' sample			
N6/10%CF	6.80	91.6	2.01
N6/20%CF	3.46	81.6	2.68
N6/30%CF	2.60	86.5	3.58
1/2'' sample			
N6/10%CF	7.57	85.9	1.82
N6/20%CF	4.22	85.4	2.41
N6/30%CF	2.51	72.6	3.20

3.3.3.4 Izod Impact Test

Table 3.13 and 3.14 show the impact resistance of nylon 6/cellulose fiber and nylon 66/cellulose fiber composites. With the adding of cellulose fiber, the impact resistance decreased. With the increase of fiber content, impact resistance decreased.

Table 3.13 Izod impact properties of nylon 6/cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N6/10%CF	4.12	0.29
N6/20%CF	3.53	0.33
N6/30%CF	3.45	0.29

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N6	8.94	0.33
N6/10%CF	3.81	0.18
N6/20%CF	3.69	0
N6/30%CF	2.30	0.22

Table 3.14 Izod impact properties of nylon 66/cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/10%CF	3.18	0.62
N66/20%CF	2.56	0.22
N66/30%CF	2.37	0.21

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66	4.84	0.40

3.3.4 Effect of binder

Polyurethane is used as binder of polyamide and cellulose fiber. Since it can react with both matrix and fiber, it will hopefully enhance the interaction between fiber and matrix, then increase the final properties.

The binder used is Hydrosize® U1-01 provided by Hydrosize Technoligies, Inc. 2% binder was mixed with the cellulose fiber. The binder is waterborne polyurethane dispersion with 55% non-volatiles. First the 55% dispersion was diluted to 10% with D.I. water, the 10% solvent was sprayed on cellulose fiber evenly. The cellulose fiber with 2% binder was dried at 100°C overnight. The treated cellulose fiber then was mixed with nylon 6 by the same extrusion-compression procedure as before. Figure 3.4 shows the reaction between polyurethane, nylon 6, and cellulose fiber.

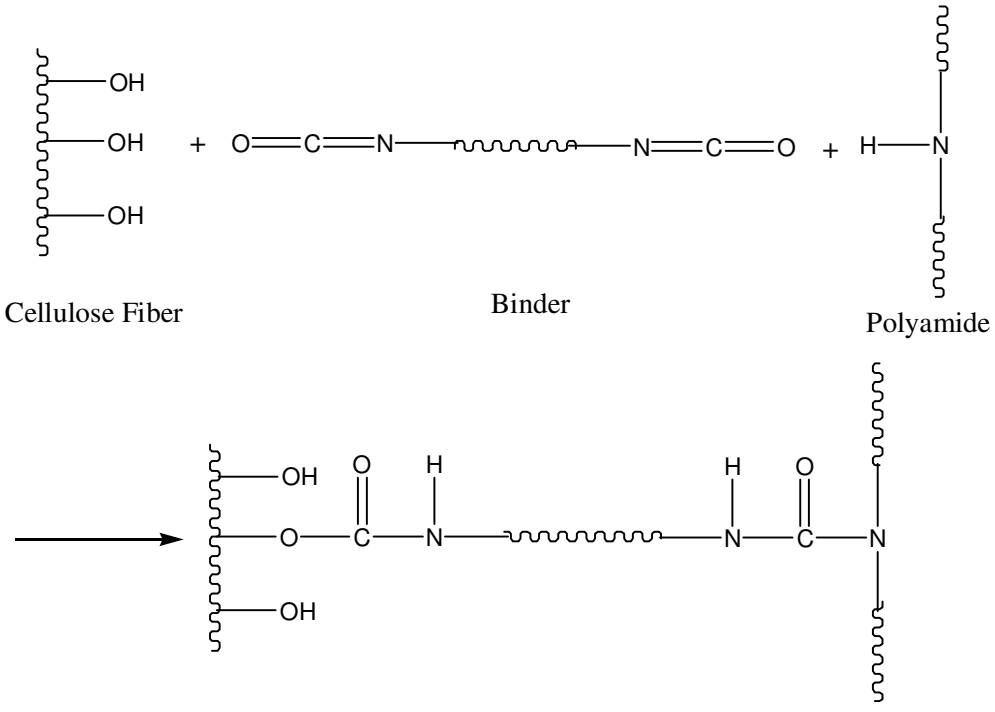


Figure 3.4 Reaction between binder, matrix and fiber

Figures 3.5-3.7 show the flexural properties of composites with and without binder. However, the binder didn't improve the properties as expected. From the results, we can't tell if the binder increases or decreases the properties. There's only a small fluctuation between the properties with or without binder. This means either nylon and cellulose fiber have very good compatibility, or the binder didn't react with the fiber and matrix.

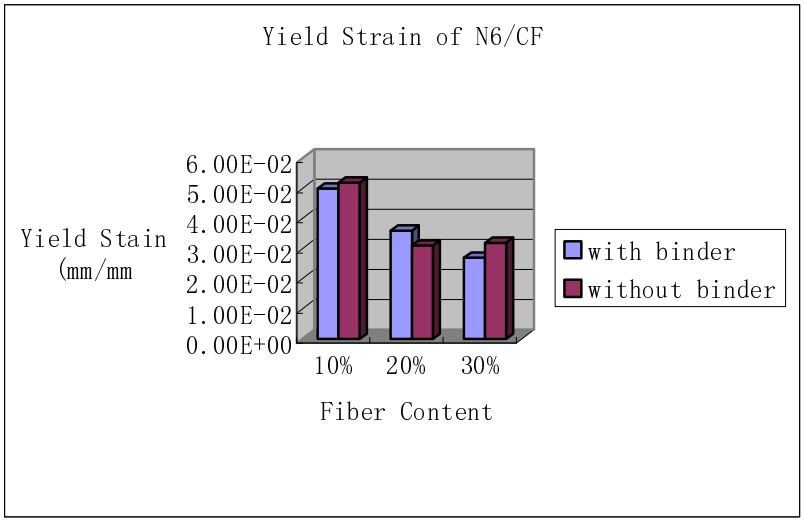


Figure 3.5 Yield stain of nylon 6/cellulose fiber with and without binder

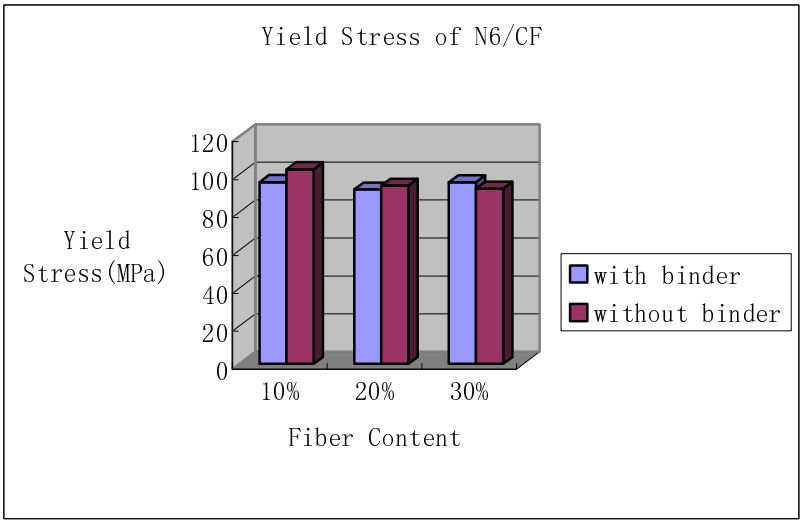


Figure 3.6 Yield stress of nylon 6/cellulose fiber with and without binder

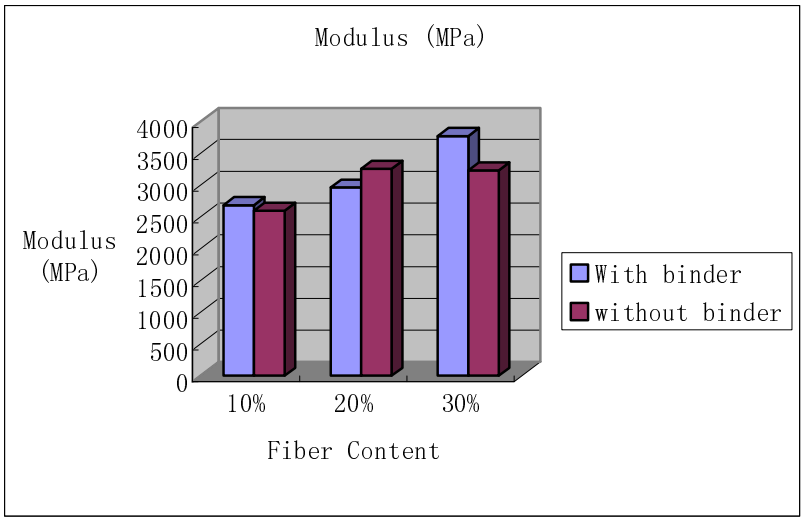


Figure 3.7 Yield stress of nylon 6/cellulose fiber with and without binder

3.3.5 Cellulose Fiber Analysis after Processing

The fiber length distribution is one of the most important factors for fiber reinforced composites. After the matrix and fiber are determined, fiber length is the adjustable factor to control the final properties of composites. Table 3.15 shows the mean fiber length for nylon 6 and nylon 66/cellulose fiber made by two processes. We can see that for nylon 6 composites, the mean fiber length after extrusion didn't decrease a lot. Injection molding clearly decreased the fiber length after extrusion. For nylon 66 composites, the fiber length is shorter than nylon 6 after extrusion, probably because of the higher temperature caused more thermal degradation of fibers, then the fibers were easier to break.

Table 3.15 Fiber length

Fiber	Mean Length (mm)	
	Arithmetic	Length weighted
TC 2500	0.292	0.539
TC 2500 in formic acid for 5 days	0.292	0.670
Extrusion		
10% CF/N6	0.258	0.515
20% CF/N6	0.236	0.468
30% CF/N6	0.226	0.441
Extrusion-Injection Molding		
10% CF/N6	0.153	0.240
20% CF/N6	0.172	0.326
30% CF/N6	0.177	0.279
Extrusion		
10% CF/N66	0.181	0.310
20% CF/N66	0.197	0.361
30% CF/N66	0.189	0.350

For cellulose fiber composite, there's another factor controlling its final properties, the thermal degradation of cellulose fiber. Figure 3.8 shows the filtered cellulose fiber from different processes. Like the color of composites samples in Figure 3.4, extrusion-compression molding gives lighter color than extrusion-injection molding, and nylon 6

composites have lighter color than nylon 66 composites. It's not easy to estimate the fiber properties with different thermal degradation.

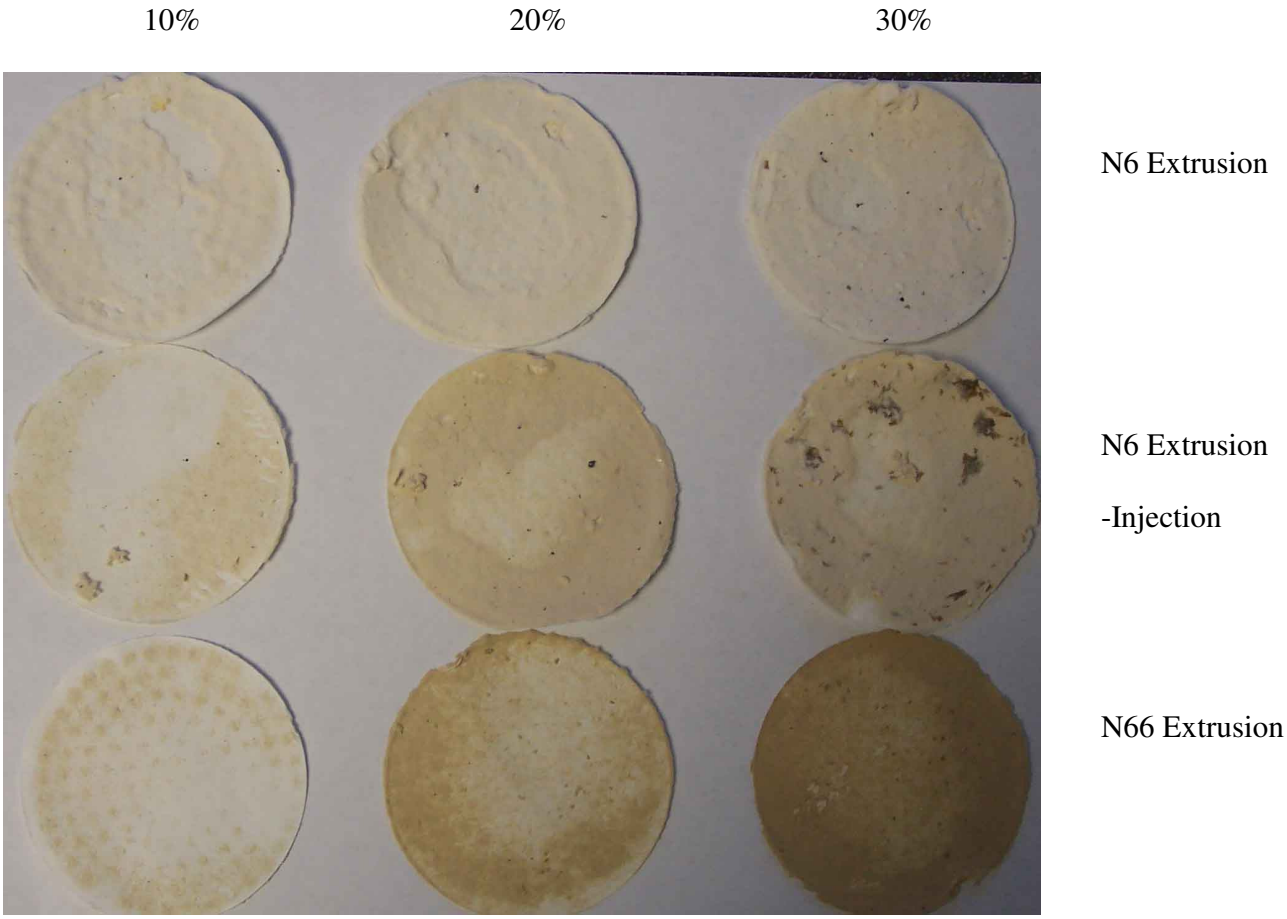


Figure 3.8 Filtered cellulose fiber

3.3.6 Morphology of composites

Figure 3.9 shows the fracture surface of nylon 6/cellulose fiber with extrusion-compression procedure. The smooth fracture surface shows that the material is brittle. Voids mean that the sample is not perfect, as discussed before. Fibers are peeled off in the fracture direction. Figure 3.10 shows an embedded fiber. There's no obvious

separation between fiber and matrix, which means that the compatibility between fiber and matrix is fine. Figure 3.11 shows the fracture surface after the fiber is peeled away. The peeled fiber implies that the interface can be improved further.

Figure 3.12 is the comparison of 10% cellulose fiber/nylon 6 fracture surface following two processes. Figure 3.12 (a) is the composite from extrusion-injection molding. Figure 3.12 (b) is the composite from extrusion-compression molding. It is clear that composite from extrusion-compression molding has longer fiber length than extrusion-injection molding, which is consistent with the measurements in Table 3.15.

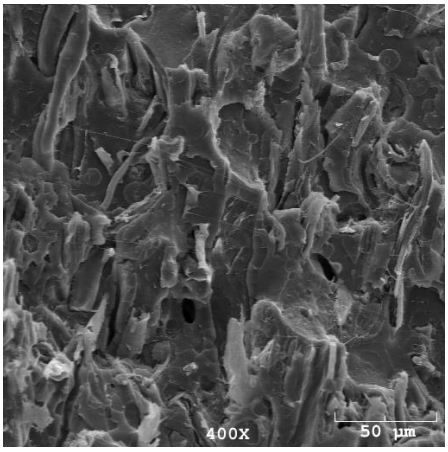


Figure 3.9 Fracture surface of 10% cellulose fiber/nylon 6

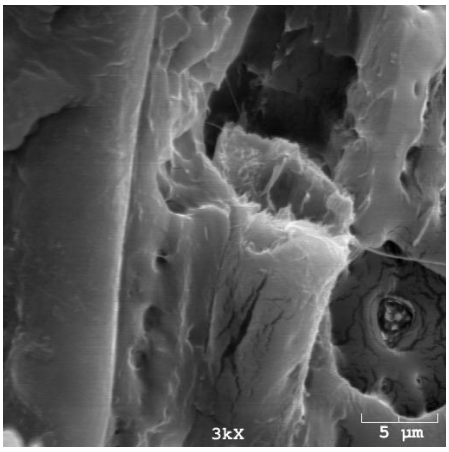


Figure 3.10 Embedded fiber

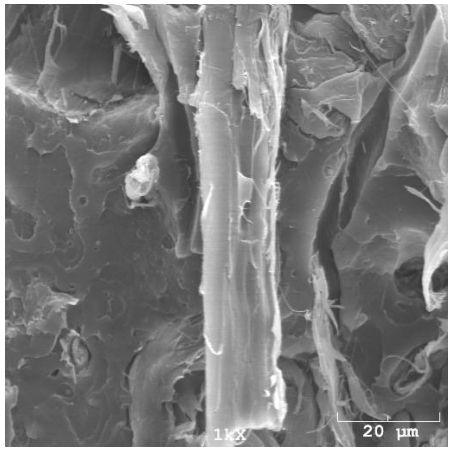
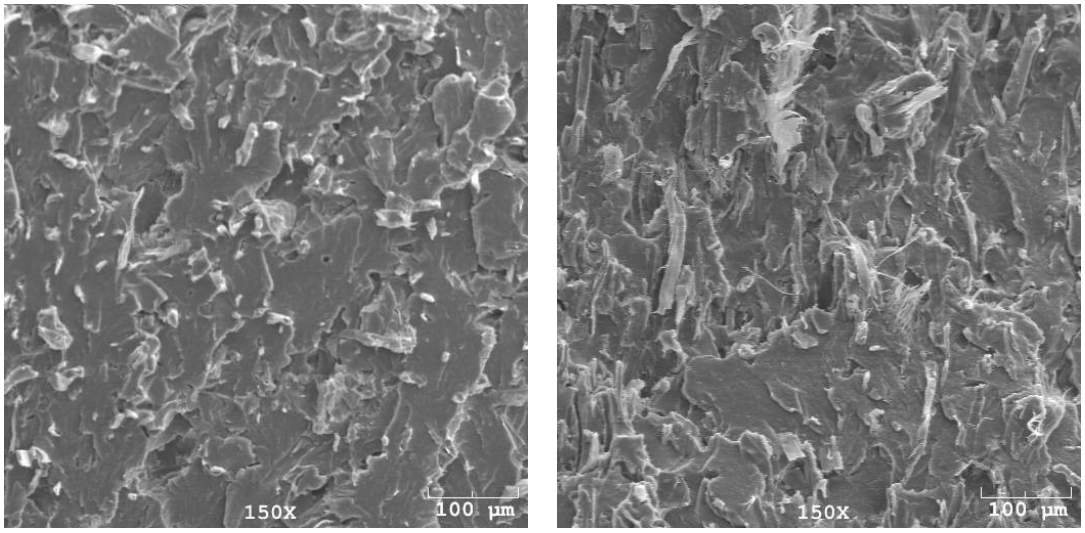


Figure 3.11 Surface after fiber peeled



(a) Extrusion-injection molding **(b) Extrusion-compression molding**

Figure 3.12 Nylon 6/cellulose fiber fracture surface made by different procedures

3.3.7 Attempt to decrease processing temperature

Thermal degradation of cellulose fiber is a big issue that affects the final properties of composites. We need to decrease the thermal degradation of cellulose fiber during processing. To get low degraded nylon/cellulose fiber composites, we can either increase the heat stability of cellulose fiber, or decrease the processing temperature.

Fiber treatments/modifications can be used to affect fiber/matrix interface, dimensional stability, biological resistance, mechanical properties, etc [2-6]. But obviously, it's easier to lower the processing temperature. Figure 3.13 shows the DSC of nylon 6. It is easy to see that after melting, when temperature decreased, polymer doesn't solidify at the same melting temperature. The solidification temperature is 20°C lower than the melting temperature, which gives us a chance to lower the processing temperature of the extruder.

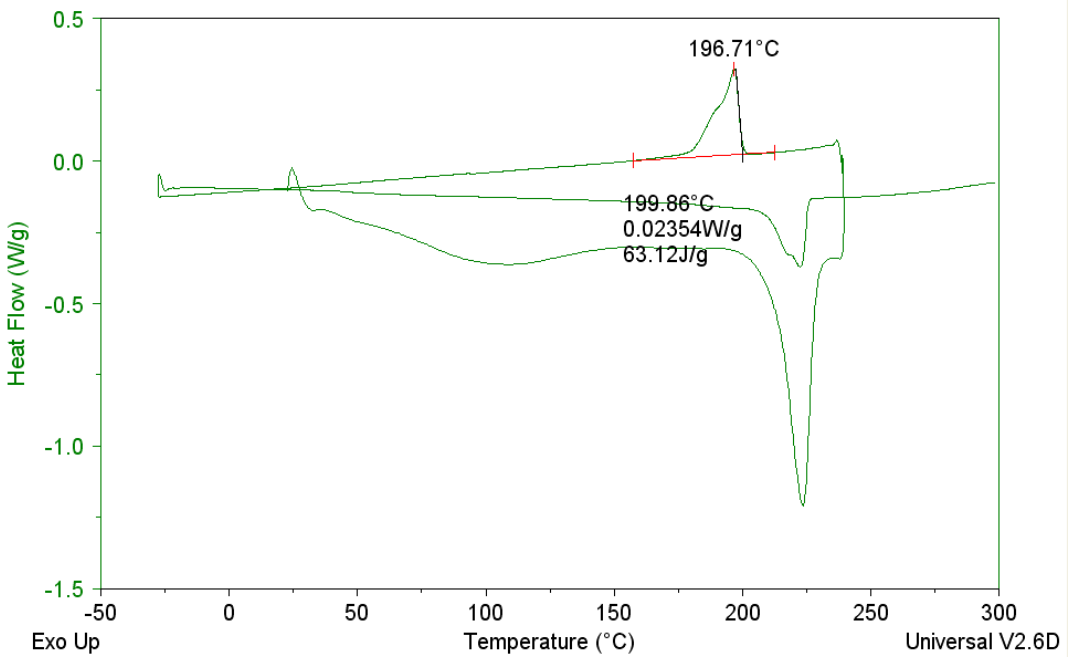


Figure 3.13 DSC of nylon 6

The processing temperature of extruder from zones 1- 6 and die is set to be 210, 230, 240, 235, 230, 220, and 210°C, respectively. The cellulose fiber is added in zone 4. For this case, if the nylon 6 pellets are melted in zones 1-3, we can decrease the temperature

from zone 4 below melting temperature to decrease the thermal degradation of cellulose fiber.

Table 3.16 and 3.17 present the adjusted temperature profiles for nylon 6 and 66/cellulose fiber composites. Table 3.18-3.23 shows the mechanical properties of nylon 6 and nylon 66/cellulose fiber composites with extrusion-compression molding and extrusion-injection molding procedures. The results show that at lower temperature, with extrusion-compression molding procedure, the tensile and flexural properties didn't get better, especially at high fiber content. There're two reasons: (1) at lower temperature, the viscosity of polymer gets higher, the fiber can't disperse in polymer very well. (2) At lower temperature, the melt polymer tends to solidify in less time when we try to collect the composite with metal plate. Before compression, part of the polymer has already been cold, thus causing more voids and defects. But with the extrusion-injection molding procedure, the modulus and stress of nylon 6/cellulose fiber composites all get significantly higher even though the temperature profile for injection molding is the same. For nylon 66/cellulose fiber composites, the injection molding can make samples from the extruded pellets. But the injection molded samples, especially for 30% cellulose fiber content composite, have very poor modulus and stress. The reason is that the fiber gets degraded too severely. For Izod impact test, with increase of fiber content, the impact resistance decreases. Extrusion-injection molded samples have lower impact resistance than compression molded samples. More research needs to be done on the cellulose fiber/nylon 66 composites.

Table 3.16 Extrusion/Injection molding temperature profiles for nylon 6/cellulose fiber

Extrusion

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
215	220	225	210	210	210	200

Injection Molding

Temperature (^{o}C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
230	230	230	210	205	38	35

Table 3.17 Extrusion/Injection molding temperature profile for nylon 66/cellulose fiber

Extrusion

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
250	255	265	240	240	240	240

Injection Molding

Temperature (^{o}C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
265	265	265	250	240	49	35

Table 3.18 Tensile properties of nylon 6/cellulose fiber composites at low temperature

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N6/10%CF (14.6%)	2.91	50.6	2.97
N6/20%CF (30.9%)	1.18	46.0	4.50
N6/30%CF (41.5%)	0.89	33.7	4.01
Extrusion-Injection Molding			
N6/10%CF (14.6%)	2.79	56.2	3.33
N6/20%CF (30.9%)	1.98	62.3	4.67
N6/30%CF (41.5%)	1.52	60.8	5.57

Standard Deviation

Extrusion –Compression Molding			
N6/10%CF (14.6%)	0.56	0.92	0.41
N6/20%CF (30.9%)	0.81	9.77	2.69
N6/30%CF (41.5%)	0.18	6.61	0.33
Extrusion-Injection Molding			
N6/10%CF (14.6%)	0.57	1.67	0.16
N6/20%CF (30.9%)	0.33	4.16	0.19
N6/30%CF (41.5%)	0.09	2.99	0.25

Table 3.19 Flexural properties of nylon 6/cellulose fiber at low temperature

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion -Compression Molding			
N6/10%CF (14.6%)	6.8	91.7	2.01
N6/20%CF (30.9%)	3.46	81.6	2.68
N6/30%CF (41.5%)	2.60	86.5	3.58
Extrusion-Injection Molding			
N6/10%CF (14.6%)	6.3	84.8	2.50
N6/20%CF (30.9%)	5.25	104.3	3.57
N6/30%CF (41.5%)	4.3	108.0	4.18

Standard Deviation

Extrusion -Compression Molding			
N6/10%CF (14.6%)	0.582	3.17	0.072
N6/20%CF (30.9%)	0.610	11.1	0.17
N6/30%CF (41.5%)	0.444	16.6	0.34
Extrusion-Injection Molding			
N6/10%CF (14.6%)	0.111	0.77	0.098
N6/20%CF (30.9%)	0.509	2.49	0.079
N6/30%CF (41.5%)	0.349	3.10	0.108

Table 3.20 Izod impact property of nylon 6/cellulose fiber at low temperature

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N6/10%CF (14.6%)	5.44	0.63
N6/20%CF (30.9%)	5.23	0.35
N6/30%CF (41.5%)	3.72	0.51

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N6	8.94	0.33
N6/10%CF (14.6%)	3.36	0.18
N6/20%CF (30.9%)	2.62	0.27
N6/30%CF (41.5%)	1.72	0.18

Table 3.21 Tensile properties of nylon 66/cellulose fiber at low temperature

Mean

Actual Fiber Content	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N66/10%CF (16.5%)	0.82	23.9	3.47
N66/20%CF (28.5%)	0.96	34.2	4.55
N66/30%CF (40%)	0.86	38.2	5.07
Extrusion-Injection Molding			
N66/10%CF (16.5%)	2.40	60.8	3.87
N66/20%CF (28.5%)	1.12	43.0	4.67
N66/30%CF (40%)	0.35	13.7	4.55

Standard Deviation

Extrusion –Compression Molding			
N66/10%CF (16.5%)	0.23	11.5	1.02
N66/20%CF (28.5%)	0.16	8.39	0.77
N66/30%CF (40%)	0.23	13.7	1.50
Extrusion-Injection Molding			
N66/10%CF (16.5%)	0.25	2.23	0.81
N66/20%CF (28.5%)	0.11	4.11	1.07
N66/30%CF (40%)	0.01	1.61	0.81

Table 3.22 Flexural properties of nylon 66/cellulose fiber composites at low temperature

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion -Compression Molding			
N66/10%CF (16.5%)	3.41	67.8	2.24
N66/20%CF (28.5%)	3.26	75.0	2.50
N66/30%CF (40%)	2.43	74.4	3.35
Extrusion-Injection Molding			
N66/10%CF (16.5%)	5.27	93.9	2.81
N66/20%CF (28.5%)	2.61	78.3	3.66
N66/30%CF (40%)	1.07	39.2	4.02

Standard Deviation

Extrusion -Compression Molding			
N66/10%CF (16.5%)	0.864	18.0	0.36
N66/20%CF (28.5%)	0.336	12.7	0.25
N66/30%CF (40%)	0.505	14.9	0.84
Extrusion-Injection Molding			
N66/10%CF (16.5%)	0.54	5.1	0.10
N66/20%CF (28.5%)	0.24	6.1	0.09
N66/30%CF (40%)	0.28	11.4	0.24

Table 3.23 Izod impact test of nylon 66/cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/10%CF (16.5%)	3.28	0.78
N66/20%CF (28.5%)	3.19	0.48
N66/30%CF (40%)	2.85	1.02

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66	4.84	0.40
N66/10%CF (16.5%)	1.89	0.19
N66/20%CF (28.5%)	1.05	0.30
N66/30%CF (40%)	0.69	0.18

3.3.8 Effects of the plasticizers / modifiers

3.3.8.1 Effects of INTEC powder

International technical polymer systems Inc ((ITPS) claimed that their product, INTEC SB 94, can decrease the processing temperature and shorten molding cycle. The INTEC SB 94 is a metallic complex based on oxides of Titanium, Aluminum, and Magnesium. The specific chemical identity and composition of the product is a trade secret so we don't know the exact components. During extrusion processing, INTEC acts as flow enhancer, and during injection molding, INTEC helps to shorten the cooling time.

This is because the INTEC SB 94 absorbs heat very efficiently; it cools the plastic resin more quickly and more uniformly.

INTEC and nylon 6 or nylon 66 was mixed in the Brabender. The mixing temperature was 240° C for nylon 6, and 280° C for nylon 66. 3% and 5% INTEC were mixed with nylon 6 and nylon 66 for 15 minutes with the screw speed of 40rpm. The mixed samples were ground to small pieces and tested by DSC and rheometer. Figure 3.14 and 3.15 show the DSC of 3% INTEC/nylon 6 and 5% INTEC/nylon 66. Surprisingly, INTEC didn't change the melting temperature of nylon 6 or nylon 66. And INTEC increased the solidification temperature. Figure 3.16 and 3.17 show the viscosity vs. shear rate of 3% INTEC/nylon 6 and 5% INTEC/nylon 66. Instead of decreasing the viscosity of nylon, INTEC increased the viscosity a little bit. The mechanism of INTEC decreasing the processing temperature is unknown. It's difficult to decide the suitable processing temperature of INTEC/nylon according to the DSC and rheology tests.

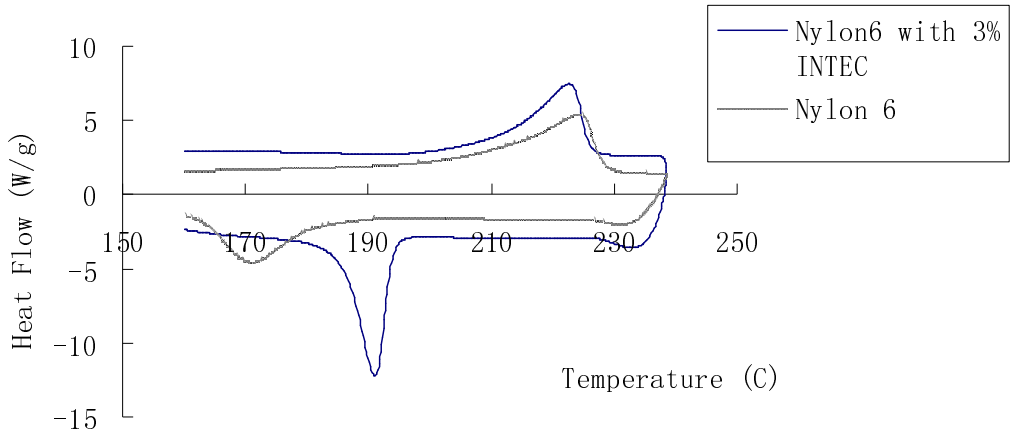


Figure 3.14 DSC of 3% INTEC/nylon 6

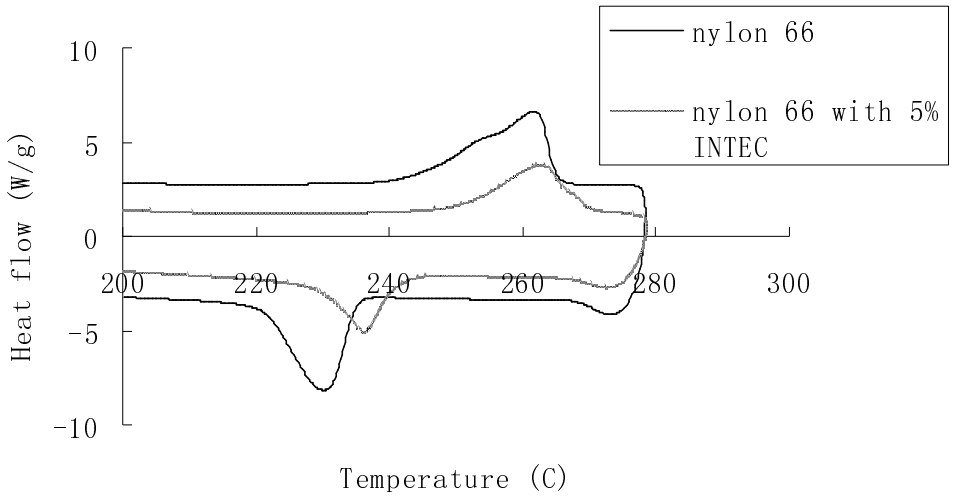


Figure 3.15 DSC of 5% INTEC/nylon 66

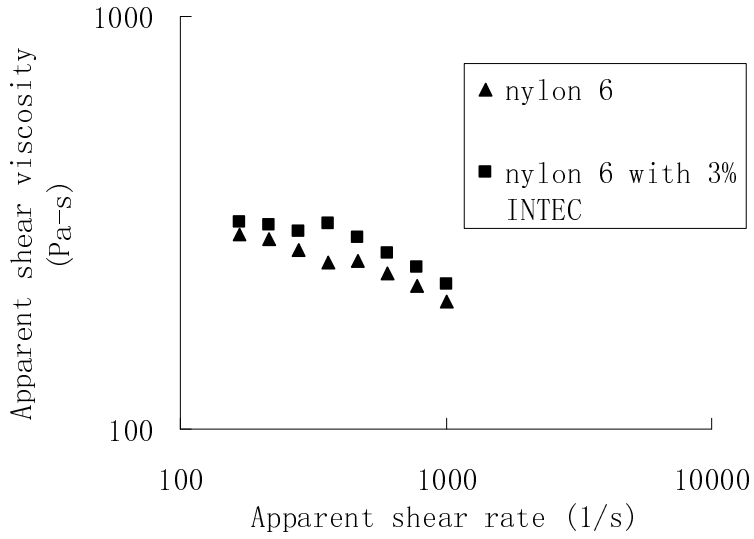


Figure 3.16 Apparent shear viscosity vs. apparent shear rate of nylon 6 and 3%INTEC/nylon 6

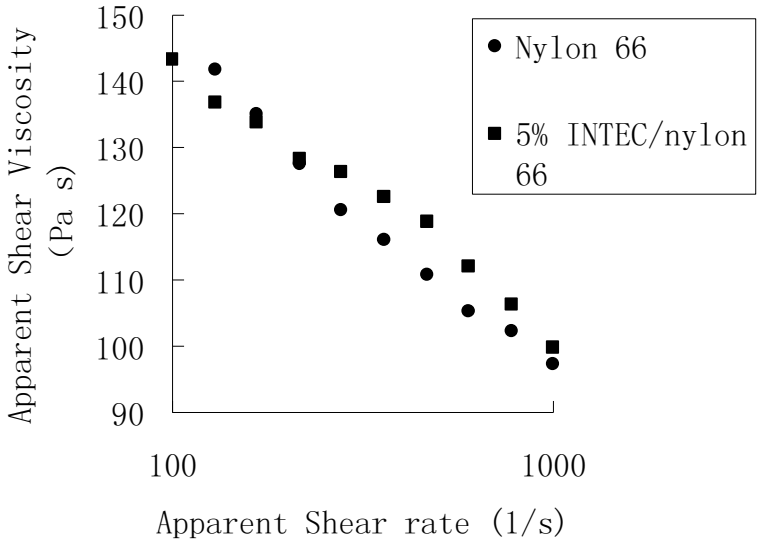


Figure 3.17 Apparent shear viscosity vs. apparent shear rate of nylon 66 and 5%INTEC/nylon 66

To determine how low the processing temperature can reach, the mixture of INTEC and nylon was fed to the extruder. 3% INTEC was mixed with nylon 6, and 5% INTEC was mixed with nylon 66 in a plastic bag then put in the feeder. The temperature of extruder was first set to be the normal processing temperature for nylon 6 or nylon 66. Then gradually decrease the processing temperature while the extruder's running. Each time drop 5℃ increments. Between each temperature adjustment run the extruder for at least 15 minutes for stabilization. Continue to drop the temperature until the lowest level was reached. Torque and melt temperature were monitored. The lowest processing temperature for nylon 6 and nylon 66 with INTEC are shown on table 3.24 and 3.25. We can see that with 3% INTEC, the temperature of nylon 6 from heating zone 4 can be

decreased to 210℃. With 5% INTEC, the temperature of nylon 66 from heating zone 4 can be decreased to 230℃.

Table 3.24 Extrusion temperature profile for 3% INTEC/nylon 6

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
210	220	225	210	210	210	210

Table 3.25 Extrusion temperature profile for 5% INTEC/nylon 66

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
245	250	255	230	230	230	230

Samples from the die of the extruder were collected and were ground into small pieces. Ground materials were injection molded to tensile and flexural samples. To decide the processing parameters of injection molding, similar procedure as extrusion was performed. The temperature of injection molding was first set to be normal temperature as nylon 6 or nylon 66, and then the temperature was gradually dropped until the lowest level reached. The cooling time was first set to be 35 seconds, same as virgin nylon 6 or nylon 66. Then the cooling time was gradually decreased until the samples in the mold get too hot. The shortest cooling time is 20 seconds. The cycle time of the injection molding then decreased from 65 seconds to 40 seconds. With the decrease of temperature and cooling time, the thermal degradation of cellulose fiber can be decreased.

Table 3.26 and 3.27 show the processing parameters of 3% INTEC/nylon 6 and 5% INTEC/nylon 66 during injection molding.

Table 3.26 Injection Molding temperature profile for 3% INTEC/nylon 6

Temperature (°C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
205	210	220	220	220	32	20

Table 3.27 Injection Molding temperature profile for 5% INTEC/nylon 66

Temperature (°C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
245	245	245	250	240	46	20

Table 3.28 Mechanical properties on nylon 6/INTEC

	Nylon 6	With 3%INTEC
Tensile Modulus (MPa)	1920	1436
Tensile Stress (MPa)	44.2	60.8
Tensile Strain (%)	26.3	22.8
Flexural Modulus (MPa)	1370	1718
Flexural Stress (MPa)	69.8	72
Flexural Strain (%)	7.36	7.37

Table 3.29 Mechanical properties on nylon 66/INTEC

	Nylon 66	With 5%INTEC
Tensile Modulus (GPa)	1.54	2.92
Tensile Stress (MPa)	66.2	57.2
Tensile Strain (%)	23	6.0
Flexural Modulus (GPa)	1.88	2.65
Flexural Stress (MPa)	77.8	98.2
Flexural Strain (%)	7.56	6.98

Table 3.28 and 3.29 show the mechanical properties of 3% INTEC/nylon 6 and 5% INTEC/nylon 66. With the INTEC, the modulus increased, strain decreases, and stress decreased a little bit. 5% INTEC changed the modulus of nylon 66 significantly.

To make INTEC/nylon/cellulose fiber composites, the mixture of INTEC and nylon was fed as matrix from the first hopper of the extruder. Cellulose fiber was fed from the middle hopper. The extrusion temperature was set the same as INTEC/nylon. The compression molding and injection molding were also used to make samples, as mentioned before. The hot mixture was collected and compressed into plaques. The mixture was ground to small pellets and injection molded. The temperature and cooling time of injection molding were determined by the INTEC/nylon trial.

To test the actual fiber content, the INTEC must be considered. INTEC can not dissolve in formic acid. However, INTEC contains nano particles. Some nano particles may pass the filter paper and drop into the formic acid during filtration. To measure how much INTEC powder will stay on the filter paper, pure INTEC powder was weighed and

put into formic acid. Then filter the mixture of INTEC and formic acid. Dry and weigh the filtered INTEC. 89% INTEC was remained on the filter paper. Weigh and put the cellulose fiber/3%INTEC/nylon 6 composites in the formic acid. The nylon 6 is dissolved, and the solution is filtered. Cellulose fiber and part of INTEC powder were filtered. Suppose the matrix contains 3% INTEC. The actual fiber content can be calculated by

$$f\% = \frac{w_{filtered} - 89\% * 3\% * w_{composite}}{w_{composite}}$$

Where $w_{filtered}$ is the weight of filtered materials. $w_{composite}$ is the weight of the composite before dissolved.

Table 3.30, 3.31 and 3.32 shows the tensile, flexural and Izod impact properties of 3% INTEC/nylon 6/cellulose fiber composites. The extrusion-injection molding procedure gives higher stress, modulus, and strain than the extrusion-compression molding procedure. The reason was explained before. Extrusion-injection molding produced samples with less voids and better fiber dispersion. The standard deviation of extrusion-injection molding samples is lower than the extrusion-compression molding. With high fiber content, stress and modulus gets higher, strain get lower for the extrusion-injection molding samples. For extrusion-compression molding samples, the properties of 30% fiber content composites is lower than 20% because of poor fiber dispersion. Injection molded samples have lower impact resistance than compression molded samples.

Table 3.30 Tensile properties of nylon 6/3%INTEC/cellulose fiber

Mean

Fiber Content	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N6/10%CF (16.3%)	1.36	51.3	3.27
N6/20%CF (22.6)	1.49	44.8	3.88
N6/30%CF (28.4%)	1.23	40.6	3.86
Extrusion-Injection Molding			
N6/10%CF (16.3%)	3.24	56.1	3.47
N6/20%CF (22.6)	2.35	62.0	4.05
N6/30%CF (28.4%)	1.99	67.7	4.96

Standard Deviation

Extrusion –Compression Molding			
N6/10%CF (16.3%)	1.44	5.3	0.418
N6/20%CF (22.6)	0.19	2.09	0.443
N6/30%CF (28.4%)	0.35	9.7	0.474
Extrusion-Injection Molding			
N6/10%CF (16.3%)	0.49	0.96	0.272
N6/20%CF (22.6)	0.43	2.44	0.250
N6/30%CF (28.4%)	0.22	1.73	0.194

Table 3.31 Flexural properties of nylon 6/3%INTEC/cellulose fiber

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N6/10%CF (16.3%)	4.9	87.3	2.59
N6/20%CF (22.6)	4.02	91.1	3.06
N6/30%CF (28.4%)	3.78	86.2	2.99
Extrusion-Injection Molding			
N6/10%CF (16.3%)	6.13	97.8	2.91
N6/20%CF (22.6)	5.3	95.3	3.09
N6/30%CF (28.4%)	4.32	99.8	3.74

Standard Deviation

Extrusion –Compression Molding			
N6/10%CF (16.3%)	0.83	6.17	0.168
N6/20%CF (22.6)	0.33	4.55	0.134
N6/30%CF (28.4%)	0.35	18.2	0.741
Extrusion-Injection Molding			
N6/10%CF (16.3%)	0.38	1.84	0.154
N6/20%CF (22.6)	0.44	3.3	0.131
N6/30%CF (28.4%)	0.19	1.60	0.211

Table 3.32 Izod impact test of nylon 6/3%INTEC/cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N6/10%CF (16.3%)	2.42	0.45
N6/20%CF (22.6)	2.33	0.15
N6/30%CF (28.4%)	2.45	0.55

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
3% INTEC/N6	4.02	0.18
N6/10%CF (16.3%)	2.21	0.19
N6/20%CF (22.6)	2.29	0.18
N6/30%CF (28.4%)	1.68	0.04

For nylon 66, the adding of INTEC can decrease the processing temperature significantly. Similar as INTEC/nylon 6/cellulose fiber composites, the 5% INTEC/nylon 66/cellulose fiber composites also used the temperature profiles as shown in Table 3.25 and 3.27. 5% INTEC was mixed with nylon 66 and fed from the first hopper. Cellulose fiber was fed from the second hopper. Hot mixture was collected and compression molded. The extruded composite was also collected, ground and injection molded to test samples.

The mechanical properties of the 5% INTEC/nylon 66/cellulose fiber of extrusion-compression molding and extrusion-injection molding are shown on Table 3.33, 3.34 and

Table 3.33 Tensile properties of nylon 66/5%INTEC/cellulose fiber

Mean

	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N66/10%CF (5.6%)	0.62	22.2	3.92
N66/20%CF (16.8%)	1.09	37.2	3.88
N66/30%CF (26%)	0.81	38.0	5.30
Extrusion-Injection Molding			
N66/10%CF (5.6%)	3.48	69.4	3.58
N66/20%CF (16.8%)	2.51	61.4	3.83
N66/30%CF (26%)	1.57	54.1	4.73

Standard Deviation

Extrusion –Compression Molding			
N66/10%CF (5.6%)	0.06	1.97	0.025
N66/20%CF (16.8%)	0.15	6.1	0.409
N66/30%CF (26%)	0.43	6.43	1.343
Extrusion-Injection Molding			
N66/10%CF (5.6%)	0.07	0.7	0.2
N66/20%CF (16.8%)	0.31	0.85	0.198
N66/30%CF (26%)	0.28	3.52	0.634

Table 3.34 Flexural properties of nylon 66/5%INTEC/cellulose fiber

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N66/10%CF (5.6%)	5.34	101	2.70
N66/20%CF (16.8%)	3.83	85.1	2.87
N66/30%CF (26%)	3.56	78.3	3.05
Extrusion-Injection Molding			
N66/10%CF (5.6%)	6.59	102.7	2.96
N66/20%CF (16.8%)	4.65	95.26	3.23
N66/30%CF (26%)	3.39	87.3	3.77

Standard Deviation

Extrusion –Compression Molding			
N66/10%CF (5.6%)	1.84	21.4	0.256
N66/20%CF (16.8%)	0.43	16.7	0.205
N66/30%CF (26%)	0.53	23.1	0.482
Extrusion-Injection Molding			
N66/10%CF (5.6%)	0.29	4.83	0.090
N66/20%CF (16.8%)	0.86	4.87	0.538
N66/30%CF (26%)	0.28	3.69	0.120

Table 3.35 Izod impact test of nylon 66/5%INTEC/cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/10%CF (5.6%)	3.07	0.71
N66/20%CF (16.8%)	2.18	0.38
N66/30%CF (26%)	2.33	0.44

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/5% INTEC	3.05	0.50
N66/10%CF (5.6%)	2.96	0.24
N66/20%CF (16.8%)	2.15	0.09
N66/30%CF (26%)	1.75	0.22

3.35. With the increase of fiber content, the tensile modulus for both extrusion-compression molding and extrusion-injection molding increases. But the tensile stress of extrusion-compression molding increases with the increase of fiber content, while stress of extrusion-injection molding decreases. This can be explained by the severe thermal degradation of cellulose fiber due to extrusion-injection molding procedure. Cellulose fiber has less thermal degradation during extrusion-compression molding procedure. Flexural stress of both extrusion-compression molding and extrusion-injection molding decreases with the increase of fiber content. This also indicates the thermal degradation is still severe even though INTEC decreased the processing temperature of nylon 66. The

actual fiber content was measured with the same method as 3% INTEC/nylon 6 composites.

3.3.8.2 Effects of plasticizers

Since we can't get satisfied products of nylon 66 by decreasing the processing temperature using the difference between solidification temperature and melting temperature or adding of INTEC, other methods need to be considered to decrease the processing temperature. Plasticizer is the traditional way to decrease the melting temperature of polymer. For polyamide, the plasticizers are usually used to modify the low temperature impact strength, toughness, fatigue life or decrease the glass transition temperature. There's no plasticizer specifically used to decrease the melting temperature of polyamide. The most commonly used plasticizer, N-butylbenzenesulfonamide (NBBSA) [7] will be tried to decrease the melting temperature of nylon 6 or 66. Also, it was reported that with chloride metal salts can decrease the melting temperature of polyamide. [8-10] Lithium chloride (LiCl) was chosen because it was reported to have the most significant effect on decreasing the melting temperature. [9] Caprolactam was reported to work as plasticizer of polyamide. Thiourea was reported to decrease the melting temperature of nylon. [10]

Plasticizer was mixed with nylon by the twin screw extruder. The extrusion temperature profiles of nylon 6 and 66 are shown on Table 3.36 and 3.37. The extruded samples were collected and ground to small pellets. The pellets were tested by DSC and rheometer. The pellets were also injection molded for tensile and flexural test.

Table 3.36 Extrusion temperature profile for nylon 6/plasticizer

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
210	220	230	240	240	240	240

Table 3.37 Extrusion temperature profile for nylon 66/plasticizer

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
250	260	270	270	270	270	270

DSC was used to identify the melting temperature and solidification temperature of mixtures. Table 3.38 and 3.39 shows the melting temperature and solidification temperature of nylon 6/plasticizer and nylon 66/plasticizer. Nylon 66 is the difficult one since it has higher melting temperature. More plasticizers were tried to decrease the melting temperature of nylon 66. It is clear that NBBSA can not decrease the melting temperature of nylon 6 but it can decrease the melting temperature of nylon 66. LiCl is very effective to decrease the melting temperature of both nylon 6 and nylon 66. 3% LiCl can decrease the melting temperature of nylon 6 from 224^{o}C to 210^{o}C. 4% LiCl can decrease the melting temperature of nylon 66 from 262^{o}C to 247^{o}C. 10% LiCl can decrease the melting temperature to 227^{o}C . Caprolactam can decrease the melting and solidification temperature of nylon 66 a little bit but not significantly. Thiourea can't decrease the melting temperature of nylon 66, either.

Table 3.38 Effect of plasticizers on the melting temperature of nylon 6

Plasticizer	None	3% LiCl	3% BBSA
Melting temperature (^{o}C)	224	210	222.5
Solidification temperature (^{o}C)	171	175	190

Table 3.39 Effect of plasticizers on the melting temperature of nylon 66

Plasticizer	None	4% LiCl	10% ε-Caprolactam
Melting temperature (^{o}C)	262	247	259
Solidification temperature (^{o}C)	230	214	231
Plasticizer	10% LiCl	6% Thiourea	4% NBBSA
Melting temperature (^{o}C)	227	259	244
Solidification temperature (^{o}C)	N/A	233	209

Table 3.40 and 3.41 shows the mechanical properties of nylon 6/plasticizer and nylon 66/plasticizer. For nylon 6, 3% LiCl doesn't affect the properties of nylon 6 much. 3% NBBSA decreased the tensile and flexural stress significantly. For nylon 66, 10% LiCl decreased the tensile modulus and stress but increased the strain significantly. . With high content LiCl, the crystallinity of nylon 66 decreased a lot, the samples were transparent after injection molding. Even though 10% LiCl can decrease the melting temperature to 227^{o} C, we still can't use it because it decreased the mechanical properties too much. 4% LiCl and NBBSA all increased the modulus of nylon 66 significantly. Low

content LiCl or NBBSA can be used to decrease the melting temperature without decreasing the mechanical properties of matrix too much.

Table 3.40 Mechanical properties on nylon 6/plasticizer

	Nylon 6	3% LiCl	3% NBBSA
Tensile Modulus (GPa)	1.92	1.47	1.62
Tensile Stress (MPa)	44.2	52.0	31.7
Tensile Strain (%)	26.3	19.8	4.09
Flexural Modulus (GPa)	1.37	1.59	1.06
Flexural Stress (MPa)	69.8	70.9	45.1
Flexural Strain (%)	7.36	7.87	8.17

Table 3.41 Mechanical properties on nylon 66/plasticizer

	Nylon 66	10% LiCl	4% LiCl	4% NBBSA
Tensile Modulus (GPa)	1.54	0.210	3.69	2.73
Tensile Stress (MPa)	66.2	19.2	41.4	65.8
Tensile Strain (%)	23.5	47.4	1.26	7.4
Flexural Modulus (GPa)	1.88	0.590	2.62	2.15
Flexural Stress (MPa)	77.8	29.1	125.5	92.1
Flexural strain (%)	7.56	8.4	6.85	7.43

Low content LiCl / nylon 6 or 66 were used as matrix. However, the extrusion didn't go smoothly even at normal processing temperature of nylon. Figure 3.18 and 3.19 show

the viscosity vs. shear rate of nylon 6/plasticizer and nylon 66/plasticizer. Surprisingly, LiCl increases the viscosity of nylon 6 and nylon 66 significantly. Figure 3.20 shows the torque of 3% NBBSA / nylon 6 and 3% LiCl/nylon 6 at extrusion temperature shown in Table 3.36. With the adding of LiCl, the torque increased significantly. With the high torque of matrix (3% LiCl/nylon 6), it's very difficult to add cellulose fiber because the adding of cellulose fiber can increase the torque 30%. The same trend can be observed for 3% LiCl/nylon 66.

LiCl can decrease the melting temperature of nylon 6 or 66 significantly without decreasing the mechanical properties of nylon at low content. It should be an ideal choice to decrease the extrusion temperature. However, LiCl can increase the viscosity of the matrix which caused difficulties to add cellulose fiber during extrusion. No more than 10% cellulose fiber can be added because of torque limitation of the extruder. No composites were made successfully with 3% LiCl/nylon 6 or 4% LiCl/nylon 66 matrix.

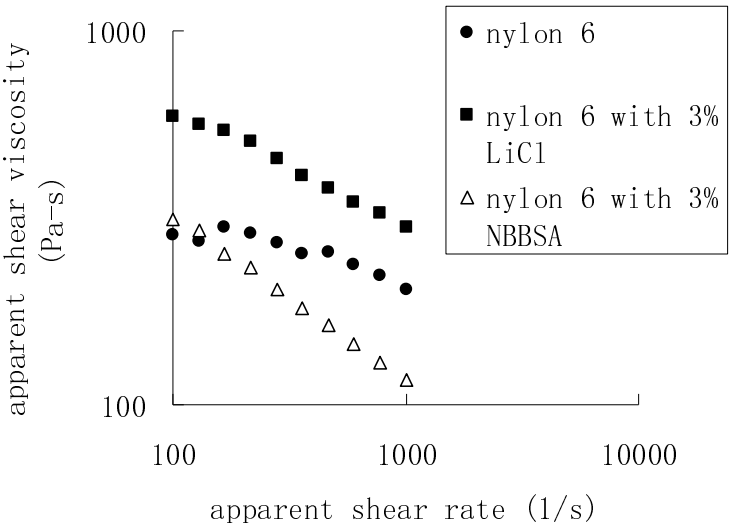


Figure 3.18 Apparent shear viscosity vs. apparent shear rate of nylon 6 and plasticizer/nylon 6 at 230° C

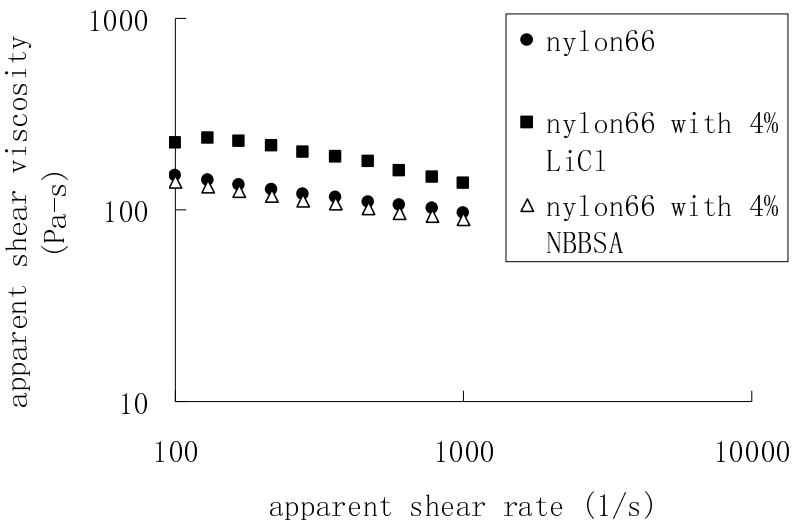


Figure 3.19 Apparent shear viscosity vs. apparent shear rate of nylon 66 and plasticizer/nylon 66 at 270° C

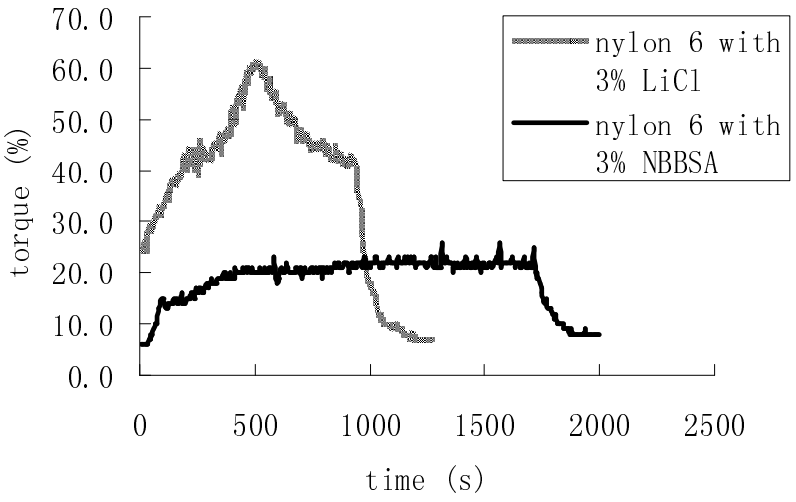


Figure 3.20 Torque during extrusion of 3% LiCl/nylon 6 and nylon 6

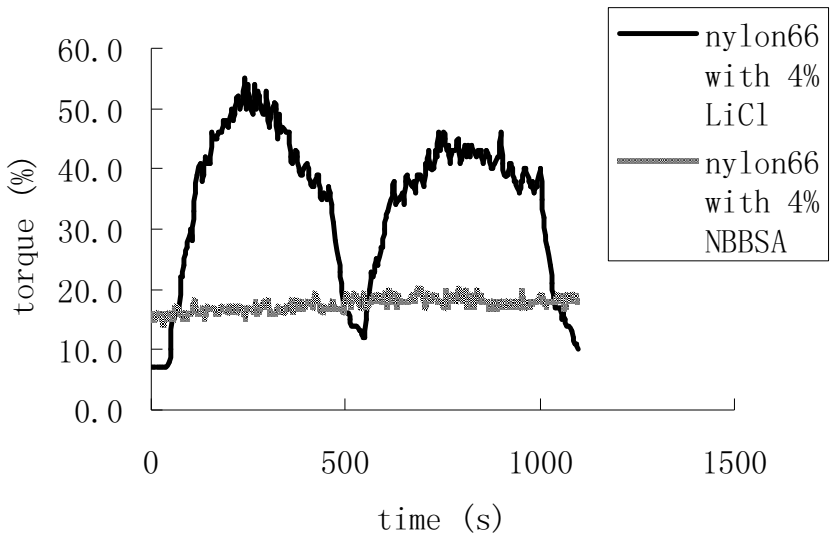


Figure 3.21 Torque during extrusion of 4% LiCl/nylon 66

3.3.8.3 Combination of plasticizer and INTEC

LiCl cannot be used as a plasticizer separately since it increases the viscosity. From Figure 3.18-3.21, NBBSA can decrease the viscosity of nylon significantly. But it can't change the melting temperature. If LiCl and NBBSA were used together, then LiCl can decrease the melting temperature while NBBSA can decrease the viscosity. The melting temperature of 3% LiCl / 3% NBBSA / nylon 66 is 251°C. 3% LiCl and 3% NBBSA were mixed with nylon 66 in plastic bag and fed from the first hopper of the extruder. The extrusion temperature profile is the same as Table 3.37. The mixture was collected from the die and ground to small pieces. Ground pellets were fed as the matrix. The extrusion temperature can be decreased to 250°C. To decrease the processing temperature further, 3% INTEC was mixed with the 3% LiCl/3% NBBSA/nylon 66 pellets as matrix. The processing temperature can be decreased more. To decide the processing temperature, the temperature was first set to 240, 250, 250, 250, 250, 250, 250

^{o}C. The temperature was decreased 5^{o}C each time. The extruder was run for at least 15 minutes until the extrusion stabilized. Then another 5^{o}C decrease was implemented andthe same operation repeated until the lowest processing temperature was reached.

Table 3.42 shows the extrusion temperature profile of 3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber composites. It is clear that the mixture has much lower processing temperature than nylon 66. The highest heating zone temperature is 240^{o}C, much lower than the melting temperature of nylon 66. After determining the processing temperature, feed 10%, 20% and 30% cellulose fiber from the second hopper. The torque was monitored carefully during adding cellulose fiber. If the torque is too high, the feeding rate of both matrix and fiber was decreased proportionally to make same fiber content composites.

Use 3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66 as matrix. Injection molding parameters were also determined by decreasing the temperature and cooling time gradually. The injection molding temperature is also much lower than virgin nylon 66. The temperature is also used for 3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ 10%, 20%, 30% cellulose fiber composites.

Table 3.42 Extrusion temperature profile for

3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
230	240	240	230	230	230	230

Table 3.43 Injection molding temperature profile for

3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber

Temperature (^{o}C)						Cooling Time (s)
Zone 1	Zone 2	Zone 3	Zone 5	Zone 6	Mold	
240	235	235	245	240	46	25

Table 3.44, 3.45 and 3.46 shows the mechanical properties of 3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber composites. With the increase of fiber content, the tensile and flexural modulus increase, while the tensile and flexural strength all decrease. This result indicates that even when the processing temperature is decreased, the thermal degradation of cellulose fiber is still severe, especially for 30% fiber content. The tensile and flexural strength of injection molded composites is higher than the compression molded samples. Izod impact test results have the same trend as others. With an increase of fiber content, impact resistance decreases.

Table 3.44 Tensile properties of

3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N66/10%CF (7.42%)	1.26	38.8	3.27
N66/20%CF (16.6%)	0.69	26.0	4.98
N66/30%CF (26.0%)	0.55	23.9	4.76
Extrusion-Injection Molding			
N66/10%CF (7.42%)	2.01	65.7	3.81
N66/20%CF (16.6%)	1.25	48.8	4.22
N66/30%CF (26.0%)	0.91	42.6	5.01

Standard Deviation

Extrusion –Compression Molding			
N66/10%CF (7.42%)	0.06	5.19	0.418
N66/20%CF (16.6%)	0.26	8.8	0.452
N66/30%CF (26.0%)	0.09	3.05	0.321
Extrusion-Injection Molding			
N66/10%CF (7.42%)	0.46	11.5	0.124
N66/20%CF (16.6%)	0.11	2.8	0.348
N66/30%CF (26.0%)	0.07	3.13	0.422

Table 3.45 Flexural properties of

3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber

Mean

(Actual Fiber Content)	Strain at Yield (%)	Stress at Yield (MPa)	Modulus (GPa)
Extrusion –Compression Molding			
N66/10%CF (7.42%)	4.93	96.2	2.61
N66/20%CF (16.6%)	4.08	105.7	3.41
N66/30%CF (26.0%)	2.31	64.9	3.45
Extrusion-Injection Molding			
N66/10%CF (7.42%)	5.37	147.0	3.75
N66/20%CF (16.6%)	3.69	127.0	4.33
N66/30%CF (26.0%)	2.22	91.9	5.16

Standard Deviation

Extrusion –Compression Molding			
N66/10%CF (7.42%)	0.59	5.2	0.281
N66/20%CF (16.6%)	0.14	10.62	0.334
N66/30%CF (26.0%)	0.43	18.89	0.526
Extrusion-Injection Molding			
N66/10%CF (7.42%)	0.60	4.98	0.0296
N66/20%CF (16.6%)	0.22	5.3	0.178
N66/30%CF (26.0%)	0.10	3.83	0.0838

Table 3.46 Izod impact properties of

3% INTEC/ 3% LiCl/ 3% NBBSA/ nylon 66/ cellulose fiber

Extrusion -Compression Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/10%CF (7.42%)	1.95	0.26
N66/20%CF (16.6%)	1.70	0.10
N66/30%CF (26.0%)	0.98	0.69

Extrusion –Injection Molding

	Mean (KJ/m^2)	Standard Deviation (KJ/m^2)
N66/plasticizer/INTEC	3.49	1.04
N66/10%CF (7.42%)	2.17	0.11
N66/20%CF (16.6%)	1.24	0.35
N66/30%CF (26.0%)	0.43	0.11

3.3.9 Statistical analysis

In this chapter, different methods and processing parameters were used to make different fiber content cellulose fiber/nylon 6 or nylon 66 composites. Extrusion-compression molding and extrusion-injection molding are two different processing methods. During extrusion, different temperature profiles were used. The matrix was modified (3% INTEC/nylon 6, 5% INTEC/nylon 66, INTEC/LiCl/NBBA/nylon 66) to decrease the processing temperature. The fiber content was changed, too. Sometimes two different treatments gave totally different properties while sometimes the difference is not

significant. The statistical analysis will to be used to tell if two treatments are significantly different, or identify which treatment is more important.

3.3.9.1 Paired comparison design

Paired comparison can be used to see if the extrusion-compression molding and extrusion-injection molding are different. For example, choose the cellulose fiber/nylon 6 under normal extrusion temperature (properties shown in table 3.9 and 3.10). The responses include tensile modulus (TM) and stress (TS), flexural modulus (FM) and stress (FS). Since the compression molding (CM) and injection molding (IM) all use the same composites from the extrusion, CM and IM can be treated as paired treatments.

Table 3.47 Paired comparison of tensile modulus of compression molding and injection molding of cellulose fiber/nylon 6

	CM (y_{i1})	IM (y_{i2})	d_i
10%	3.01	3.12	0.11
20%	4.16	4.32	0.16
30%	4.58	5.15	0.57

The methods in a paired comparison experiment can be compared by using the paired *t* statistic:[12]

$$t_{paired} = \sqrt{N}\,\bar{d}/s_d$$

Where $d_i = y_{i2} - y_{i1}$ is the difference between the two treatments and $\bar{d} = \frac{1}{N}\sum d_i$,

$s_d = \left\{ \frac{1}{N-1} \sum \left(d_i - \bar{d}\right)^2 \right\}^{1/2}$ are the sample mean the standard deviation of the d_i.

The two methods are declared to be significantly different at the level α if

$$\left|t_{paired}\right| > t_{N-1,\alpha/2}$$

For our case $t_{paired}=1.92<t_{3\text{-}1,\ 0.05/2}=4.303$

which means the two methods are not significantly different.

Or we can calculate the *p* value. The *p* value gives the probability that the two methods are not significantly different under level α. The smaller the *p* value, the more different the two methods are. For the following analysis, we choose α=0.05. If $p<0.05$, we claim that the factor is significant.

$$p = porb(\left|t_2\right| > 1.92) = 0.195$$

The p value is larger than 0.05 so the two methods are not significantly different.

However, this method only used the average modulus of 10%, 20% and 30% cellulose fiber/nylon 6. For more accurate result we need to count all 5 test results of each fiber content composite.

3.3.9.2 Two-way layout

To count all 5 samples for each fiber content composite, the fiber content need to be treated as a factor, too. If more than one treatment is involved, the paired comparison doesn't work. Two-way layout is suitable for comparison involves two treatment factors.

The Analysis Of Variance or ANOVA table of the two way layout is shown on Table 3.48 [12]

Table 3.48 ANOVA Table for Two-Way Layout [12]

Source	Degrees of Freedom (*df*)	Sum of Squares (*SS*)	Mean Squares (*MS*)	F
A	*I-1*	$nJ\sum_{i=1}^{I}(\bar{y}_{i\cdot\cdot}-\bar{y}_{\cdots})^2$	SS_A/df_A	MS_A/MS_r
B	*J-1*	$nI\sum_{j=1}^{J}(\bar{y}_{\cdot j\cdot}-\bar{y}_{\cdots})^2$	SS_B/df_B	MS_B/MS_r
A×*B*	*(I-1)(J-1)*	$n\sum_{i=1}^{I}\sum_{j=1}^{J}(\bar{y}_{ij\cdot}-\bar{y}_{i\cdot\cdot}-\bar{y}_{\cdot j\cdot}+\bar{y}_{\cdots})^2$	SS_{AB}/df_{AB}	MS_{AB}/MS_r
Residual (*r*)	*IJ(n-1)*	$\sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{l=1}^{n}(y_{ijl}-\bar{y}_{ij\cdot})^2$	SS_r/df_r	
Total	*IJn-1*	$\sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{l=1}^{n}(y_{ijl}-\bar{y}_{\cdots})^2$		

Where y_{ijl} is the observation for the *l*th replicate of the *i*th level of factor A and the *j*th level of factor B. Factor A has I levels. B has J levels. There're n replicates for each treatment.

P value for method A=prob($F_{I-1,\,(I-1)(J-1)}>F_A$)

P value for method B=prob($F_{J-1,\,(I-1)(J-1)}>F_B$)

The small p value indicates the significant difference.

We still use cellulose fiber/nylon 6 under normal extrusion temperature (properties shown in Tables 3.9 and 3.10) as example. The data form becomes:

Table 3.49 Comparison of tensile modulus of compression molding and injection molding of cellulose fiber/nylon 6

	CM (y_{i1l})	IM (y_{i2l})
14.8% (y_{1jl})	2631.07	3281.08
	3008.51	2844.89
	3145.92	3059.62
	3358.35	3200.34
	2900.9	3308.7
28.4% (y_{2jl})	3634.19	4412.21
	5374.95	3591.77
	3423.56	3998.42
	4400.6	5446.47
	3980	4154.96
34.2% (y_{3jl})	5672.85	5528.9
	3815.43	5209.3
	5337.61	5256.58
	4813.15	4982.72
	4681.93	5349.13

For Table 3.49, *A* is the fiber content, *B* is the molding method. *I = 3, J = 2, n=5*. The ANOVA table of tensile modulus vs. molding method and fiber content was calculated by MINITAB and shown in Table 3.50. The p value indicates that fiber content changes modulus significantly, while molding methods (compression molding and injection molding) have no significant effects on tensile modulus.

Table 3.50
Two-way ANOVA: Tensile Modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	395847	395847	1.37	0.253
Fiber Content	2	20014924	10007462	34.62	0.000
Interaction	2	111149	55574	0.19	0.826
Error	24	6937795	289075		
Total	29	27459714			

The difference between compression molding and injection molding of each procedure is shown in Table 3.51. Tensile modulus, stress and strain are chosen to be responses. Molding method and fiber content are factors. For each comparison, there're three p values, one for molding method, one for fiber content, another one for interactions. The p values of molding method and fiber content are shown in Table 3.51. The p value indicates if the two molding methods are significantly different, or if the fiber content makes significant difference for tensile strength, modulus or strain.

For tensile modulus, compression molding and injection molding have no significant difference except the 3% INTEC/nylon 6/cellulose fiber composite. For 3% INTEC/nylon 6/cellulose fiber composite, the tensile modulus from injection molding is higher than compression molding. For other composites compression molding and injection molding give the same tensile modulus. Fiber content has an important affect on the tensile modulus. With the increase of fiber content, the tensile modulus increases for both compression molding and injection molding.

For tensile strength, compression molding and injection molding are significantly different except the nylon 6/cellulose fiber composite from normal extrusion temperature. Fiber content significantly affects the tensile strength. However, the trend of tensile strength with fiber content is different. For nylon 6/cellulose fiber composite under normal extrusion temperature, the compression molding and injection molding have no significant difference on tensile strength. For compression molding, with increase of fiber content, tensile strength doesn't change a lot. For injection molding, with increase of fiber content, tensile strength increases. For nylon 6/cellulose fiber composite under low extrusion temperature, the compression molding gave lower tensile strength than

injection molding. For compression molding, with increase of fiber content, tensile strength decreases. For injection molding, with increase of fiber content, tensile strength increases. For 3% INTEC/nylon 6/cellulose fiber composite, the compression molding gave lower tensile strength than injection molding. For compression molding, with increase of fiber content, tensile strength decreases. For injection molding, with increase of fiber content, tensile strength increases. For nylon 66/cellulose fiber composite under low extrusion temperature, compression molding gave lower tensile strength than injection molding for 10% fiber content while higher tensile strength for 30% fiber content. For compression molding, with increase of fiber content, tensile strength increases. For injection molding, with increase of fiber content, tensile strength decreases. For 5% INTEC/nylon 66/cellulose fiber content, compression molding gave lower tensile strength than injection molding. For compression molding, with increase of fiber content, tensile strength increases. For injection molding, with increase of fiber content, tensile strength decreases. For plasticizer/nylon 66 composites, compression molding gave lower tensile strength than injection molding. For compression molding, with increase of fiber content, tensile strength decreases. For injection molding, with increase of fiber content, tensile strength decreases.

For tensile strain, compression molding and injection molding gave different results. Fiber content affects the tensile strain significantly. For all the composites, compression molding gave lower tensile strain than injection molding. With increase of fiber content, tensile strain decreases.

The details of the change are shown in Table 3.52. > means compression molding gave higher properties than injection molding. < means compression molding gave lower

properties than injection molding. = means there's no significant difference between compression molding and injection molding. ↑ means with increase of fiber content, property increases. ↓ means with increase of fiber content, property decreases. ↔ means fiber content doesn't change property significantly.

Generally, for tensile modulus, there's no significant difference between compression molding and injection molding. With increase of fiber content, modulus increases. For tensile strain, compression molding gave lower values than injection molding. With increase of fiber content, strain decreases. Tensile strength is more complex. Generally, compression molding gave lower value than injection molding except for nylon 66 composites. The 30% cellulose fiber / nylon 66 has higher tensile strength from compression molding than injection molding. This can be explained by the extremely severe thermal degradation of cellulose fiber. For nylon 6 composite from compression molding, with increase of fiber content, tensile strength decrease. This can be explained by the poor fiber dispersion in the matrix. With fiber content increase, fiber tends to gather together in nylon 6 thus cause poor strength. For nylon 6 composites from injection molding, with increase of fiber content, tensile strength increases because fiber dispersed better in the matrix. For nylon 66 composites from injection molding, with increase of fiber content, tensile strength decreases. This can be explained by the thermal degradation of cellulose fiber. Even though fiber dispersed better, the severe thermal degradation caused fiber properties to decrease.

Table 3.51 Comparison between injection molding and compression molding (CM vs. IM)

		Tensile Modulus		Tensile Strength		Tensile Strain	
		CM vs. IM	Fiber content	CM vs. IM	Fiber content	CM vs. IM	Fiber content
CF/nylon 6, normal temp	p value	0.253	0.000	0.821	0.047	0.011	0.000
	Significant?	No	Yes	No	Yes	Yes	Yes
CF/nylon 6, low temp	p value	0.258	0.030	0.000	0.014	0.024	0.000
	Significant?	No	Yes	Yes	Yes	Yes	Yes
CF / 3% INTEC/nylon 6	p value	0.001	0.000	0.000	0.006	0.000	0.003
	Significant?	Yes	Yes	Yes	Yes	Yes	Yes
CF/nylon 66, Low temp	p value	0.291	0.013	0.000	0.000	0.000	0.000
	Significant?	No	Yes	Yes	Yes	Yes	Yes
CF/5% INTEC/nylon 66	p value	0.474	0.000	0.000	0.080	0.000	0.000
	Significant?	No	Yes	Yes	Yes	Yes	Yes
CF / 3% INTEC / plasticizer /nylon 66	p value	0.855	0.000	0.000	0.000	0.000	0.000
	Significant?	No	Yes	Yes	Yes	Yes	Yes

Table 3.52 Comparison details between injection molding and compression molding (CM vs. IM)

	Tensile Modulus			Tensile Strength			Tensile Strain		
	CM vs. IM	Fiber content		CM vs. IM	Fiber content		CM vs. IM	Fiber content	
		CM	IM		CM	IM		CM	IM
CF/nylon 6, normal temp	=	↑	↑	=	↔	↑	<	↓	↓
CF/nylon 6, low temp	=	↑	↑	<	↓	↑	<	↓	↓
CF / 3% INTEC/nylon 6	<	↑	↑	<	↓	↑	<	↓	↓
CF/nylon 66, Low temp	=	↑	↑	< for 10%; > for 30%	↑	↓	<	↓	↓
CF/5% INTEC/nylon 66	=	↑	↑	<	↑	↓	<	↓	↓
CF/3% INTEC/plasticizer/nylon 66	=	↑	↑	<	↓	↓	<	↓	↓

3.3.9.3 Analysis of Covariance

We also want to identify the difference between different processing parameters and matrix. Choose the normal temperature processing and low temperature processing of nylon 6/cellulose fiber composites, as discussed in sections 3.2.1 and 3.3.7, as an example. Temperature profile is the treatment factor, mechanical properties are the responses. Also we've known that the fiber content is an important factor, this factor can't be ignored. The fiber content couldn't be controlled precisely. The actual fiber contents vary from different extrusion. It should be treated as a covariate - it's not related to the factor, temperature, but it can affect the final properties. Choose the tensile strength from extrusion-injection molding as the response. The data sheet is shown on table 3.53. The processing temperature is one factor, fiber content is the covariance, and tensile strength is the response. The purpose of the analysis is to determine whether different processing temperature will affect the tensile stress significantly.

The analysis of covariance is the combination of regression and ANOVA. The key point here is to adjust the response data for the covariate by regressing, then doing an ANOVA on the adjusted response data.

The adjusted Y values and means are: [12]

$$y_{ij(adj)} = y_{ij} - \beta(x_{ij} - x) = \mu + \alpha_I + \varepsilon_{ij}$$

$$\mu_{i(adj)} = \mu_i - \beta(x_i - x)$$

Where β is the combined regression coefficient; x is the mean value of the covariant; y_{ij} is the jth replicate observation of the response variable; x_{ij} is the covariate value for the jth replicate observation from the ith level of factor A; μ is the mean value of response variable; ε_{ij} is the unexplained error; $\alpha_I = \mu_I - \mu$.

Table 3.53 Comparison of CF/N6

by normal temperature and low temperature extrusion

Normal Temperature		Low Temperature	
Tensile stress	Fiber content	Tensile stress	Fiber content
48.80	13.3%	58.06	14.6%
48.24	13.3%	53.87	14.6%
49.37	13.3%	56.09	14.6%
48.77	13.3%	57.55	14.6%
48.72	13.3%	55.54	14.6%
52.10	25.0%	64.15	30.9%
55.22	25.0%	64.39	30.9%
53.91	25.0%	55.35	30.9%
55.91	25.0%	61.73	30.9%
53.70	25.0%	65.87	30.9%
54.81	33.3%	65.21	41.5%
53.82	33.3%	59.88	41.5%
55.07	33.3%	59.52	41.5%
54.29	33.3%	61.95	41.5%
54.02	33.3%	57.26	41.5%

The ANOVA table for ANCOVA is shown in Table 3.54. The *I* is the number of treatments. *n* is the number of replicates.

Table 3.54 ANOVA table for ANCOVA [12]

Source	Degrees of Freedom (*df*)	Mean Squares (*MS*)	F
A (adjusted)	*I-1*	$SS_{A(adj)}/df_A$	$MS_{A(adj)}/MS_{r(adj)}$
B (covariance)	*1*	$SS_{B(adj)}/df_B$	$MS_{B(adj)}/MS_{r(adj)}$
Residual (*adjusted*)	*I(n-1)-1*	$SS_{r(adj)}/df_r$	
Total (*adjusted*)	*In-2*		

Table 3.55 shows the result of the ANCOVA. The p values of fiber content and temperature indicate that both extrusion temperature and fiber content are important for the tensile stress.

Table 3.55 General Linear Model: tensile stress versus temperature

Analysis of Variance for tensile stress, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	277.38	142.72	142.72	20.85	0.000
temperature	1	266.26	266.26	266.26	38.90	0.000
Error	27	184.82	184.82	6.85		
Total	29	728.46				

The difference between processing conditions and matrix is shown in Tables 3.56 and 3.56. Tensile modulus, stress, strain, flexural modulus, and strain are chosen to be responses. Four pairs of treatments are compared. The comparison includes: cellulose fiber/nylon 6 with normal temperature extrusion *vs.* cellulose fiber/nylon 6 with low temperature extrusion; cellulose fiber/nylon 6 with low temperature extrusion *vs.* 3% INTEC/nylon 6/cellulose fiber composites; cellulose fiber/nylon 66 with low temperature extrusion *vs.* 5% INTEC/nylon 66/cellulose fiber composites; 5% INTEC/nylon

66/cellulose fiber composites *vs.* 3% INTEC/3% LiCl/3% NBBSA/nylon 66/cellulose fiber composites. Fiber content is the covariant. The purpose of the analysis is to determine if the four pairs of treatments are significantly different. The samples made from compression molding (CM) and injection molding (IM) are compared separately.

The details of the comparison are shown in Table 3.58. ↔ means there's no significant difference between the two treatments. > means the latter treatment gives better property than the former one. < means the latter treatment gives lower property than the former treatment.

For compression molded cellulose fiber/nylon 6 with normal temperature extrusion *vs.* cellulose fiber/nylon 6 with low temperature extrusion, normal temperature extrusion gave better tensile strength and flexural modulus than low temperature extrusion. There's no significant difference between the two treatments for tensile modulus, tensile strain and flexural strength. The injection molded cellulose fiber/nylon 6 with low temperature extrusion gave better tensile strength, flexural modulus and strength than cellulose fiber/nylon 6 with high temperature extrusion.

For cellulose fiber/nylon 6 with low temperature extrusion *vs.* 3% INTEC/nylon 6/cellulose fiber composites, the compression molded cellulose fiber/nylon 6 with low temperature extrusion gave higher tensile strain and lower flexural modulus than 3% INTEC/nylon 6/cellulose fiber composites. Other properties remain the same. The injection molded 3% ITNEC/nylon 6/cellulose fiber gave higher tensile modulus, strength, flexural modulus and strength than cellulose fiber/nylon 6 with low extrusion temperature.

For cellulose fiber/nylon 66 with low temperature extrusion *vs.* 5% INTEC/nylon 66/cellulose fiber composites, the compression molded 5% INTEC/nylon 66/cellulose fiber composites have higher tensile modulus, strength, flexural modulus and strength than cellulose fiber/nylon 66 with low temperature extrusion. Injection molded 5% INTEC/nylon 66/cellulose fiber composites have higher flexural modulus than cellulose fiber/nylon 66 with low temperature extrusion.

The compression molded 5% INTEC/nylon 66/cellulose fiber composites and 3% INTEC/3% LiCl/3% NBBSA/nylon 66/cellulose fiber composites have similar properties. Injection molded plasticizer/nylon 66/cellulose fiber composites have higher tensile modulus, flexural modulus and strength than injection molded INTEC/nylon 66/cellulose fiber composites.

Generally, injection molded cellulose fiber/nylon 6 with lower extrusion temperature gave better properties than injection molded cellulose fiber/nylon 6 with normal extrusion temperature. Injection molded 3% INTEC/nylon 6 gave better properties than injection molded cellulose fiber/nylon 6 with lower extrusion temperature. Compression molded 5% INTEC/nylon 66/cellulose fiber composites have better properties than compression molded cellulose fiber/nylon 66 with low temperature extrusion. Injection molded plasticizer/nylon 66/cellulose fiber composites have better properties than injection molded INTEC/nylon 66/cellulose fiber composites.

From Table 3.52, injection molding gave better strength than compression molding. We can conclude that 3% INTEC/nylon 6/cellulose fiber composites have the best mechanical properties in nylon 6 matrix composites. With increase of fiber content, modulus and strength increase, strain decreases. 3% INTEC/3% LiCl/3% NBBSA/nylon

66/cellulose fiber composites have the best mechanical properties for nylon 66 matrix composites. With increase of fiber content, modulus increases; strength decreases; and strain decreases.

Table 3.56 Comparison between different processing parameter and matrix (Injection Molding)

		Nylon 6/CF normal temp vs. low temp		Nylon 6 low temp vs. 3% INTEC/nylon 6		Nylon 66 low temp vs. 5% INTEC/nylon 66		5% INTEC/ nylon 66 vs. plasticizer/nylon 66	
		treatment	Fiber content	treatment	Fiber content	treatment	Fiber content	treatment	Fiber content
Tensile Modulus	p value	0.357	0.000	0.034	0.000	0.369	0.003	0.022	0.000
	significant?	No	Yes	Yes	Yes	No	Yes	Yes	Yes
Tensile Strength	p value	0.000	0.000	0.047	0.002	0.164	0.000	0.001	0.000
	significant?	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Tensile Strain	p value	0.861	0.000	0.669	0.000	0.373	0.000	0.000	0.000
	significant?	No	Yes	No	Yes	No	Yes	Yes	Yes
Flexural Modulus	p value	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	significant?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Flexural Strength	p value	0.000	0.000	0.01	0.000	0.418	0.000	0.000	0.000
	significant?	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes

Table 3.57 Comparison between different processing parameter and matrix (Compression Molding)

		Nylon 6/CF normal temp vs. low temp		Nylon 6 low temp vs. 3% INTEC/nylon 6		Nylon 66 low temp vs. 5% INTEC/nylon 66		5% INTEC/ nylon 66 vs. plasticizer/nylon 66	
		treatment	Fiber content	treatment	Fiber content	treatment	Fiber content	treatment	Fiber content
Tensile Modulus	p value	0.554	0.014	0.183	0.000	0.016	0.001	0.953	0.000
	significant?	No	Yes	No	No	Yes	No	No	Yes
Tensile Strength	p value	0.005	0.000	0.625	0.000	0.001	0.000	0.272	0.560
	significant?	Yes	Yes	No	Yes	Yes	Yes	No	No
Tensile Strain	p value	0.819	0.000	0.015	0.000	0.111	0.022	0.422	0.540
	significant?	No	Yes	Yes	Yes	No	Yes	No	No
Flexural Modulus	p value	0.000	0.000	0.001	0.000	0.001	0.000	0.108	0.000
	significant?	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes
Flexural Strength	p value	0.198	0.008	0.737	0.871	0.000	0.872	0.609	0.005
	significant?	No	Yes	No	No	Yes	No	No	No

Table 3.58 Comparison details between different processing parameter and matrix

	Nylon 6/CF normal temp vs. low temp		Nylon 6 low temp vs. 3% INTEC/nylon 6		Nylon 66 low temp vs. 5% INTEC/nylon 66		5% INTEC/ nylon 66 vs. plasticizer/nylon 66	
	CM	IM	CM	IM	CM	IM	CM	IM
Tensile Modulus	↔	↔	↔	>	>	↔	↔	>
Tensile Strength	<	>	↔	>	>	↔	↔	<
Tensile Strain	↔	↔	<	↔	↔	↔	↔	<
Flexural Modulus	<	>	>	>	>	>	↔	>
Flexural Strength	↔	>	↔	>	>	↔	↔	>

3.4 References

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CHAPTER 4

STUDY OF EXTRUSION CONDITIONS

Many processing parameters will affect the properties of final products. For extrusion, processing temperature, screw speed, feeding rate, and fill ratio will all affect the properties of composites. For the same matrix and fiber, the mechanical properties of composites are determined by fiber content, fiber length, fiber orientation, and thermal degradation of cellulose fiber. Screw speed, feeding rate and fill ratio will change fiber length distribution by influencing the shear rate and residence time. Also, screw speed, feeding rate and fill ratio are not independent factors, they will interact with each other. Temperature profiles will change thermal degradation of cellulose fiber. Actual temperature of composites will also affect fiber length distribution by changing the viscosity of the molten polymer. The actual melt temperature was determined by the set temperature, viscosity of melt, etc. Details of the effects of processing parameters will be discussed in this chapter.

4.1 Actual melt temperature

The thermal degradation of cellulose fiber is one of the most important factors to determine the final properties of composites. Actual temperature of fiber in the extruder directly determines the thermal degradation. However, the actual temperature is different from the set temperature as shown in the temperature profile Table in chapter 3. With the adding of cellulose fiber, the viscosity of the melt increased significantly. Figure 4.1 shows the viscosity change with different fiber content. The increase of the viscosity caused increase of melt temperature because of the viscous heat generation.

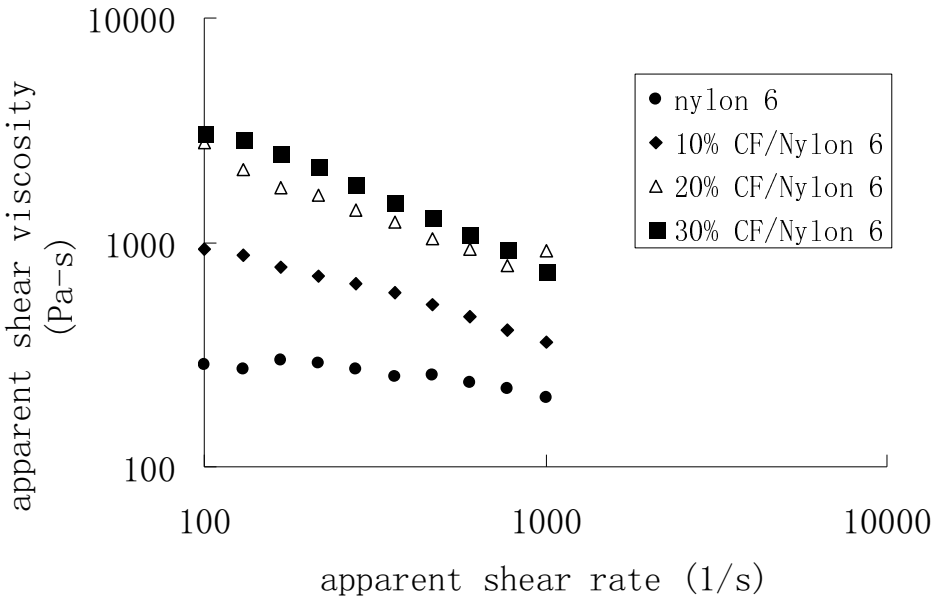

Figure 4.1 Viscosity change with different fiber content

The energy conservation, for a controlled volume is:

Net rate of gain of thermal energy = rate of thermal energy convected in + rate of thermal energy conducted in+ rate of thermal energy generation. [1]

For the simplest case of unidirectional shear, the rate of viscous heat generation per unit volume is:

$\dot{w} = \frac{1}{2}\underline{\underline{\tau}} : \underline{\underline{\dot{\gamma}}} = \eta\dot{\gamma}^2$,[2] where η is the viscosity. The viscosity depends on the shear rate, temperature and pressure. At the same shear rate, with higher viscosity, the viscous heat generation rate increases. For extrusion, the polymer flow is more complicated. It would be difficult to calculate the exact number.

Figure 4.2 shows the schematic of the twin screw extruder. In addition to the temperature setting of the six heating zones and the die, there are thermocouples inside

the barrels to measure the actual temperature of the molten polymer. In barrel 2, 5, 7, 9 and die, 5 thermocouples measure the temperature of the melt in different positions. The matrix was fed from barrel 1, and cellulose fiber was fed from barrel 6. The actual melt temperature may be different with the setting temperature.

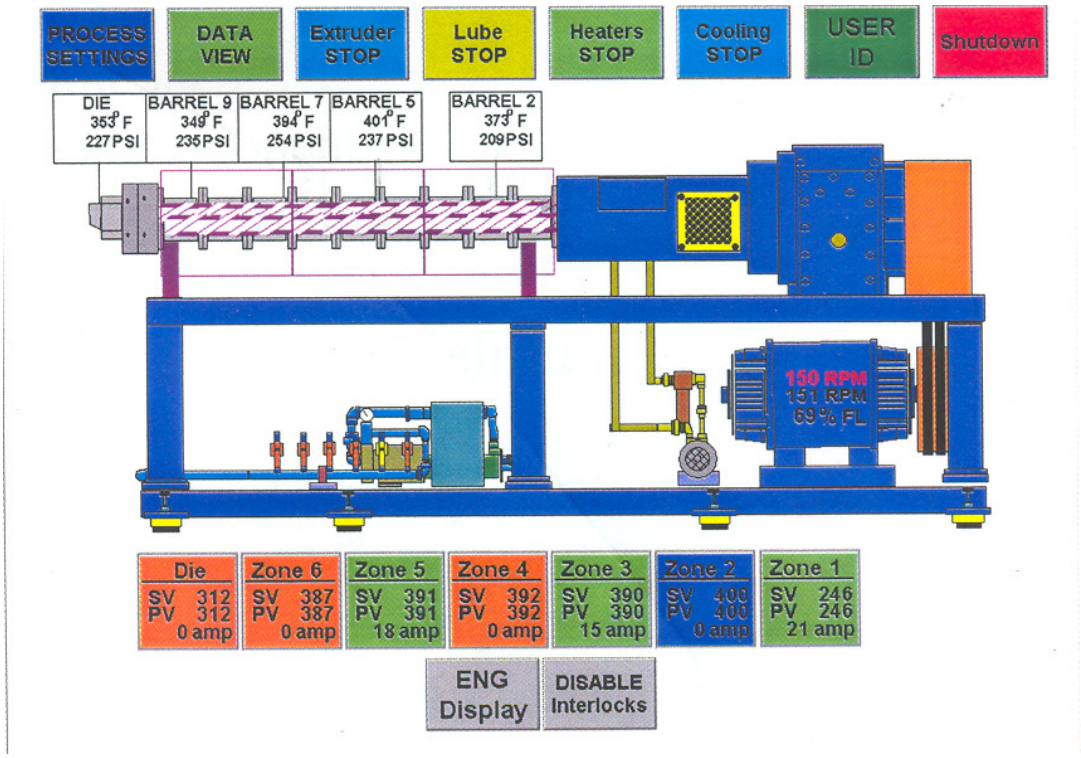

Figure 4.2 Schematic of the twin screw extruder

For the most simple processing, extrusion of 3% LiCl/2% NBBSA/nylon 6, the setting temperature is 210, 220, 230, 240, 240, 240, 240° C. Figure 4.3 shows the actual temperature measured from barrel 2, 5, 7, 9 and die. When the extruder is stopped, the melt temperature remained the same as setting temperature. When molten polymer filled in the barrel, temperature changed. The actual temperature of barrel 2 doesn't increase while feeding polymer. However, the actual melt temperatures in barrel 5, 7, 9 and the

die are higher than the set temperature. For barrel 5, the actual temperature is 245° C instead of 230° C, actual temperature of barrel 7, 9 and die is between 250 and 260° C, much higher than the set temperature, 240° C. After extrusion, the temperature in the barrel drops to the set temperature. This temperature increase is caused by the viscous heating.

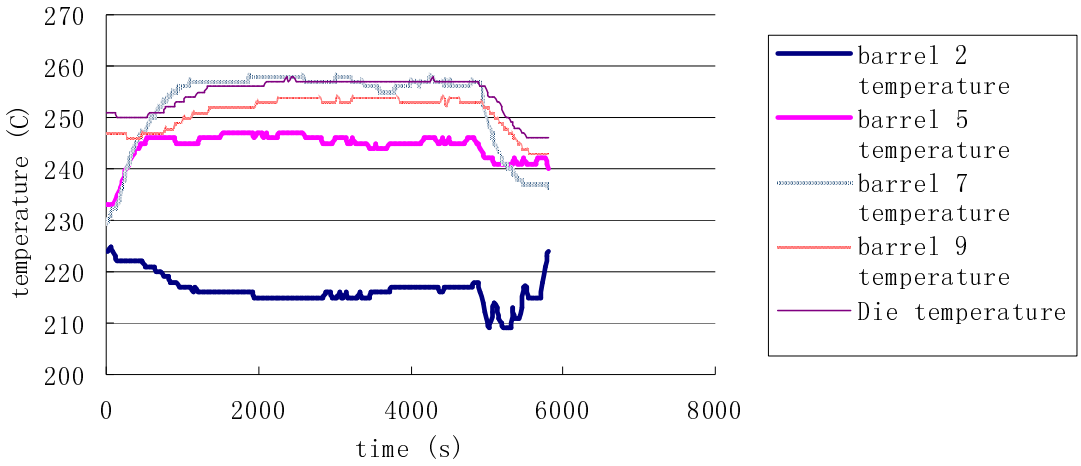

Figure 4.3 Actual temperature profile during processing of LiCl/NBBSA/Nylon 6

With cellulose fiber, the viscosity increases, and we can expect that the temperature will increase, too. Choose INTEC/nylon 66/cellulose fiber as example. As discussed in chapter 3 the setting temperature of the heating zones is 245, 250, 255, 230, 230, 230, 230° C. Figure 4.4 shows the temperature change with adding of cellulose fiber during extrusion. We can see that with the feeding of polymer, the melt temperature in barrel 5 increased from 255 to 265° C. The melt temperature dropped to 252° C in barrel 7,then dropped to 247° C in barrel 9 because the temperature from barrel 6 was set to be 230° C. Because we fed cellulose fiber from barrel 6, the actual temperature in barrel 5 kept

stable without interruption of the fiber. With adding of cellulose fiber, the melt temperature in barrel 7, 9 and die all increased. The higher the fiber content, the more the temperature increased. From Figure 4.1 we can see that with higher fiber content, the viscosity get higher, too. The increase of viscosity caused the increase of temperature. The temperature change in barrel 7 is the most obvious because fiber was fed from barrel 6. With adding of 10% cellulose fiber, melt temperature increased to 253° C, 20% fiber increased the melt temperature to 259° C, and 30% fiber increased temperature to 264° C. The temperature difference in barrel 9 and die is not as significant as barrel 7.

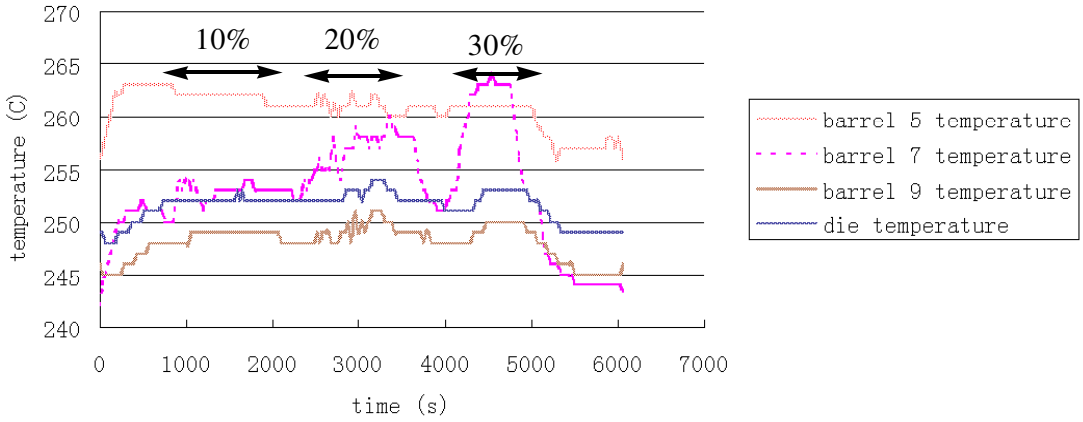

Figure 4.4 Temperature change during extrusion of 5% INTEC/nylon 6/cellulose fiber

Figure 4.4 shows that the actual melt temperature can be very different with the set temperature. The thermal history of cellulose fiber in the extruder is very complex. The actual temperature increases with the increase of fiber content. This can explain why the 30% fiber content composite has more thermal degradation than 10% composites and thus explain why 30% CF/nylon 66 has lower strength than 10% CF/nylon 66.

4.2 Residence time

Residence time is considered to be the time that polymer stays in the extruder.[3] For cellulose fiber/nylon composites, the residence time of cellulose fiber will influence the final properties. First, the residence time will affect the thermal degradation of cellulose. The longer the cellulose fiber stays in the extruder, the more thermal degradation happens. Secondly, the residence time will affect the mixing. Longer residence time will cause better mixing. Thirdly, the residence time will affect the fiber length. Under same shear rate, temperature and viscosity, longer residence time will cause shorter fiber length. Shorter residence time will cause less thermal degradation but bad mixing and longer fiber length. Longer residence time will improve the mixing but cause more thermal degradation. The affect of residence time on extrusion-compression molding procedure is unknown. For extrusion-injection molding processing, since polymer and fiber will be mixed again in injection molding, and injection molding will shorten fiber length, during extrusion the thermal degradation of cellulose fiber is the dominant factor.

To decrease thermal degradation, the residence time needs to be shortened. A lot of work has been done on the residence time analysis. [4-8] Kao and Allison [7] found that the mean residence time decreased nonlinearly with increasing screw speed and feeding rate. Feeding rate has the largest effect on the mean residence time and screw speed has a secondary effect. The barrel temperature has no effect. Chen, Patterson and Dealy[8] found that if the extruder was partially filled, the mean residence time decreased linearly with increasing screw speed. Todd [9] presented the following equation of residence time while the extruder is running starved:

$$t_m = 2L / ZN$$

Where L is the barrel length, and Z is the lead length, which ranges from 0.25 to 1.5D. N is the screw speed.

Gasner, Bigio and Marks[10] found a correlation between the residence time, screw speed and feeding rate by experiments. The model of Chen and Todd doesn't fit their experimental data.

$$t_m = \frac{A}{Q} + \frac{B}{N},$$

where Q is the feeding rate, N is the screw speed, A and B are constants for specific screw configurations.

Gao, Walsh and Bigio [4] present the following equations for A and B:

$$A = A_f L_m + V_p$$

$$B = \frac{2A_f L_c}{(2i-1)\pi D \cos\theta WHF_d}$$

Where L_c is the length of the partially filled conveying section, L_m is the length of the mixing section and melting section, V_p is the filled volume in the conveying section due to pressure back flow, i is the number of screw lobes, A_f is the free cross sectional area of the screw, D is the diameter of the screw, W is the channel width and H is the channel height.

They start with the definition of the mean residence time as the ratio between filled volume and volumetric flow rate:

$$t_m = \frac{V_f}{Q}$$

The filled volume can be divided into three sections: the filled volume in the conveying section without pressure flow (V_d), The filled volume in the conveying section

due to pressure flow (V_p), and the filled volume in the melting region (V_m). The authors assumed the melting zones are fully filled because of the reverse pumping effect of the reverse flighted elements. In the solid conveying section the filled volume (V_d) is the total free volume (V_{fc}) times the ratio of the filled ratio (flow rate (Q) divided by maximum flow rate capacity (Q_d)).

$$t_m = \frac{V_m}{Q} + \frac{V_d}{Q} + \frac{V_p}{Q}$$

$$V_m = A_f L_m$$

$$V_d = \frac{V_{fc} Q}{Q_d}$$

where $Q_d = \frac{2i-1}{2} \pi DN \cos\theta WHF_d$

Substituting V_m and V_d in the calculation equation of t_m yields the expression for A and B.

Now it is clear that *A/Q* is determined by the fully filled regions and *B/N* is determined by the partially filled regions. For our case, the cellulose fiber was fed from the middle of the extruder, where the polymer was completely melted. It is reasonable to suppose that the regions with cellulose and nylon were almost filled. And for most of the experiments the screw speed was set to be 200rpm. The residence time is mostly determined by Q.

4.3 Torque limit

Power of the extruder is determined by the shear rate, viscosity, and speed.[9]

Power = (shear rate)(viscosity)(shear area)(radius)(speed)

The extruder is powered by a 25HP A.C. motor. Torque limit sometimes restricts the parameter settings. The extruder is equipped with a torque limiting coupling between the main drive motor and the extruder gearbox. If the torque reached 100%, the extruder will shut down. During extrusion, we must pay attention to the torque. Warning will show if the torque reaches 80%.

Adding of cellulose fiber will increase the torque significantly by changing the viscosity. Figure 4.5 shows the change of torque with adding 10%, 20% and 30% cellulose fiber. 5% INTEC/nylon 66 is the matrix. We cans see that with adding of 30% cellulose fiber the torque will increase 30-40%. Thus for the matrix only, the torque needs to be under 50%.

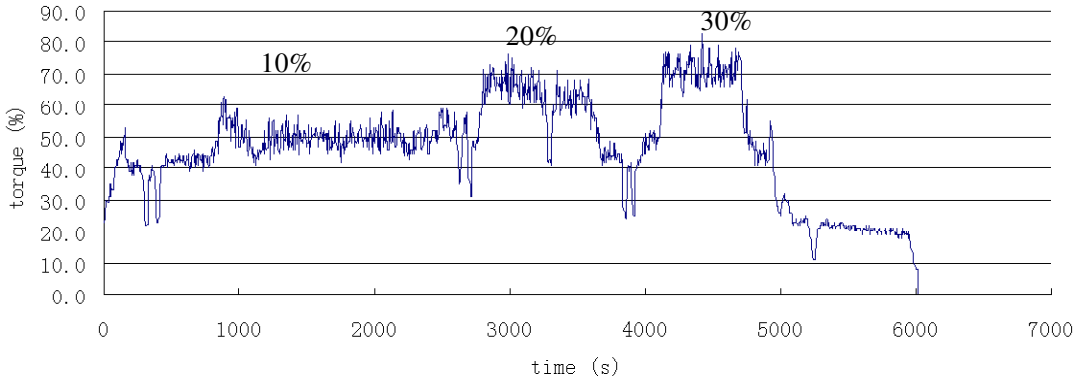

Figure 4.5 Change of torque

Temperature will affect the viscosity, and thus affect the torque. While decreasing the temperature, the viscosity of polymer increased, thus increasing the torque. Feeding rate will also affect the torque. With an increase in feeding rate torque increases. Figure 4.6 shows the torque at different temperatures and different feeding rates. High temperature is what we used for the processing before. 210, 230, 240, 235, 230, 220, and 210°C. Low temperature is: 200, 210, 225, 225, 220, 220, and 210°C. We can see that

with decrease of temperature, torque increases. With increasing feeding rate torque increases. The feeding rate determines the residence time, thus affects the thermal degradation. Temperature profile is another main factor to affect thermal degradation. Because of the torque limit we can't decrease the temperature or residence time without limitation.

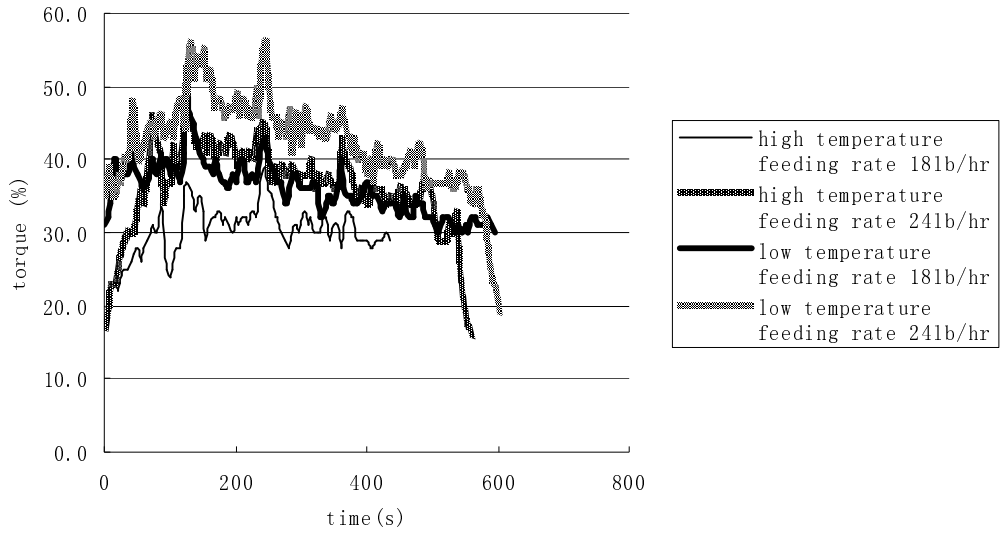

Figure 4.6 Extrusion torque of nylon 6 at different temperature and feeding rate

The torque limit determines how low the temperature can reach. In Chapter 2 USDA Forest Products Lab and Rayonier Inc. used low temperature compounding (LTC) to produce cellulose pulp fiber/PA-6 composites. They decreased the temperature of heating zones 4-7 to 149^{o} C when processing nylon 6. In our trial the lowest temperature we can reach is 210^{o} C for nylon 6.

Screw speed will also affect the torque by changing the viscosity. With the increasing screw speed viscosity decreases and thus torque decreases. Figure 4.7 shows the change of torque with the change of screw speed. With the increase of screw speed, torque decreased slightly.

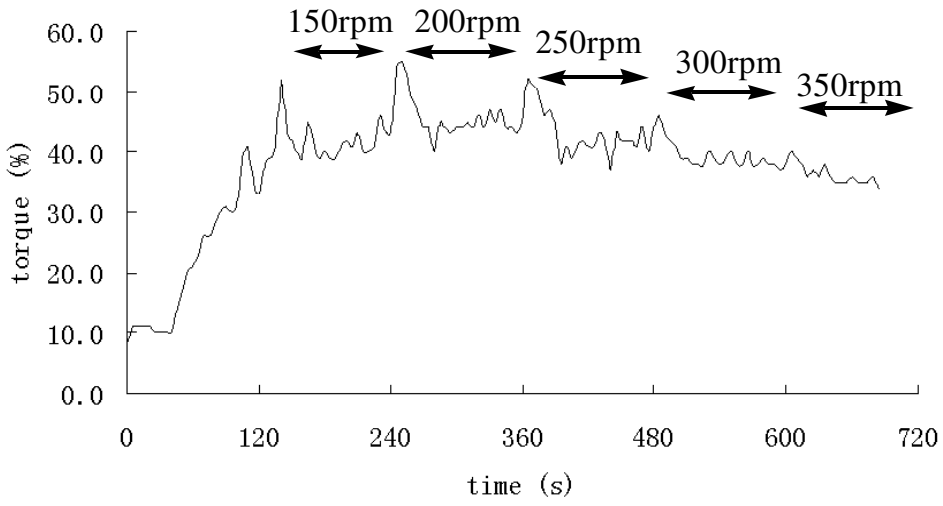

Figure 4.7 Extrusion torque of nylon 6 at different screw speed

In some cases the torque limit restricts the processing. For 3% LiCl/nylon 6 matrix, the processing temperature can be decreased to 190, 200, 210, 190, 190, 190, 190^{o} C. But the processing couldn't continue because of high torque. Feeding rate was decreased to decrease the torque, but the residence time became very long and fiber was degraded severely.

4.4 Extrusion parameters and actual melt temperature

Tables 4.1-4.7 show the extrusion parameters, including set temperature, screw speed, feeding rate, the actual melt temperature and torque during extrusion of cellulose

fiber/nylon 6 or 66 composite. Since fiber starts to feed in barrel 6, the temperature from barrel 7 indicates the thermal history of cellulose fiber. Screw speed and feeding rate determines the residence time. All the screw speeds were set to be 200rpm except the plasticizer/nylon 66 composites, which means feeding rate is the key factor to determine residence time. Feeding rate was adjusted to keep torque under 80% during extrusion. Figures 4.8-4.14 show the torque and barrel 7 temperature during extrusion. It is clear that during feeding fiber, the torque increases, and temperature of barrel 7 increases, too.

Compare the actual melt temperature and torque during processing of nylon 6 composites, as shown on Table 4.2-4.4. For all the three processing, with the increase of cellulose fiber content, actual temperature in barrel 7 increases. There's not much difference in barrel 9 and die for one setting temperature. With lower set temperature, the actual melt temperature is lower, too. However, for 3% INTEC/nylon 6 matrix, even though the set temperature is the lowest, the actual temperature is higher than the set temperature. With increase of fiber content, the torque increases under same feeding rate. With lower temperature, torque increases. 3% INTEC/nylon 6 gave highest torque because INTEC can increase the viscosity of nylon. During extrusion of 30% cellulose fiber/3% INTEC/nylon 6, the feeding rate needs to be decreased to satisfy the torque limit.

For the nylon 66 composites, the extrusion parameters and actual melt temperature are shown on Table 4.5-4.8. The trends are similar to the nylon 6 composites. With lower set temperature, actual melt temperature decreases. INTEC can increase the viscosity of nylon 66. The feeding rate of 5% INTEC/nylon 66 composites is decreased to satisfy the torque limit, and thus increases the residence time of fiber in the extruder. Table 4.8 shows that the plasticizer can decrease the actual melt temperature significantly. However,

the feeding rate needs to be very low to keep the torque under 80% because the LiCl can increase the viscosity. An extruder with a more powerful motor may make processing the cellulose fiber/plasticizer/nylon 66 composites with low set temperatures and high feeding rate feasible.

Table 4.1 Nylon 6/cellulose fiber, normal temperature

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
210	220	230	235	240	230	200	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N6	CF
10%	230	238	242	225	227	57%	180	20
20%	225	240	244	228	230	59%	160	40
30%	227	241	245	224	226	61.9%	140	60

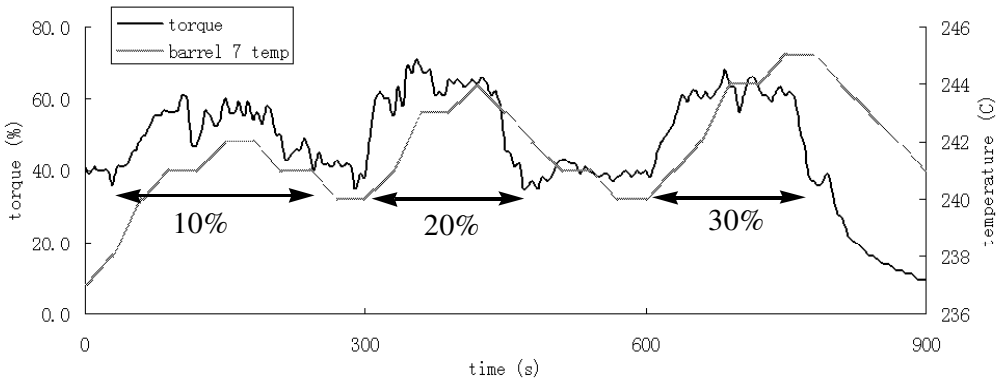

Figure 4.8 Torque and barrel 7 temperature of Nylon 6/cellulose fiber during normal temperature extrusion

Table 4.2 Nylon 6/cellulose fiber, low temperature

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
215	220	225	210	210	210	200	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N6	CF
10%	223	234	223	222	223	69.1	180	20
20%	236	238	223	222	223	74.7	160	40
30%	214	234	225	226	226	75.2	136	58

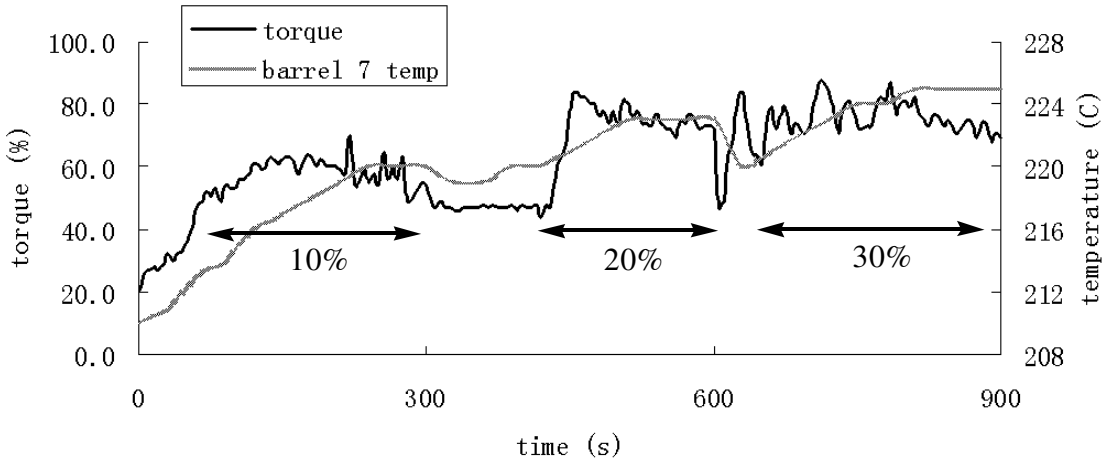

Figure 4.9 Torque and barrel 7 temperature of Nylon 6/cellulose fiber during low temperature extrusion

Table 4.3 3% INTEC/nylon 6/cellulose fiber

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
210	220	225	210	210	210	210	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N6	CF
10%	223	236	238	230	233	71.2	180	20
20%	225	234	242	231	234	71.7	136	34
30%	227	234	247	231	234	69.7	80	34

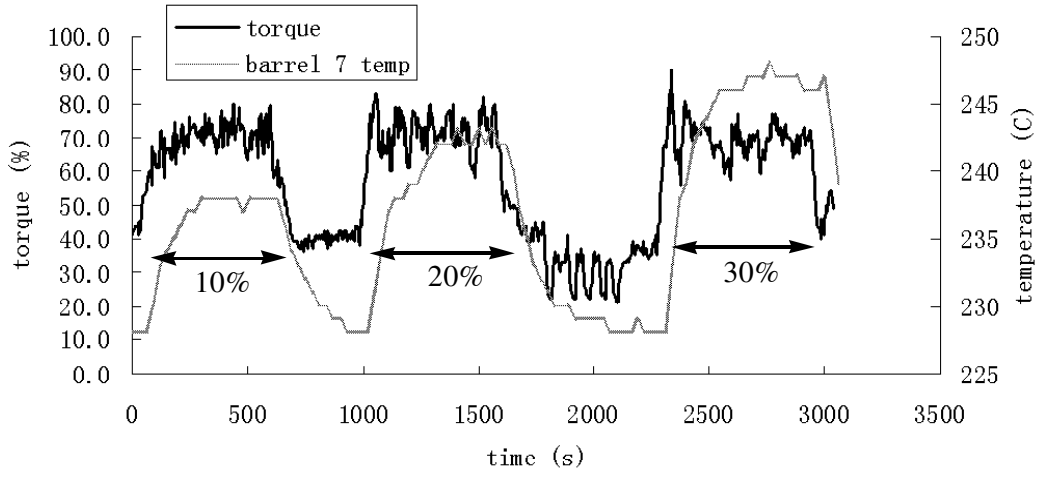

Figure 4.10 Torque and barrel 7 temperature of 3% INTEC/nylon 6/cellulose fiber during extrusion

Table 4.4 Nylon 66/cellulose fiber, normal temperature

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
250	260	265	270	270	270	240	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N66	CF
10%	257	262	268	257	258	49.0	180	20
20%	258	263	269	256	257	54.8	160	40
30%	254	263	269	255	257	58.7	135.4	58

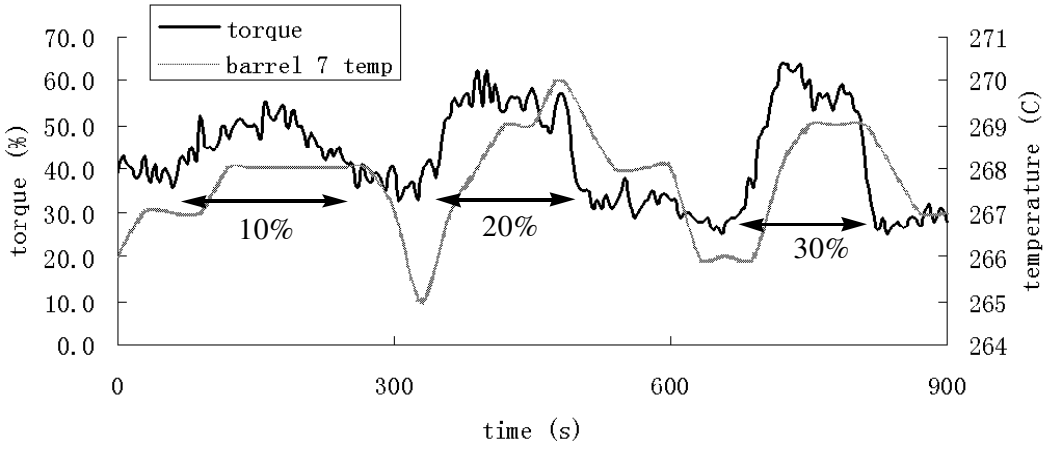

Figure 4.11 Torque and barrel 7 temperature of Nylon 66/cellulose fiber during normal temperature extrusion

Table 4.5 Nylon 66/cellulose fiber, low temperature

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
250	255	265	240	240	240	240	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N66	CF
10%	260	266	248	253	255	43.1	180	20
20%	260	266	249	256	258	43.9	160	40
30%	260	266	250	256	258	50.0	135.4	58

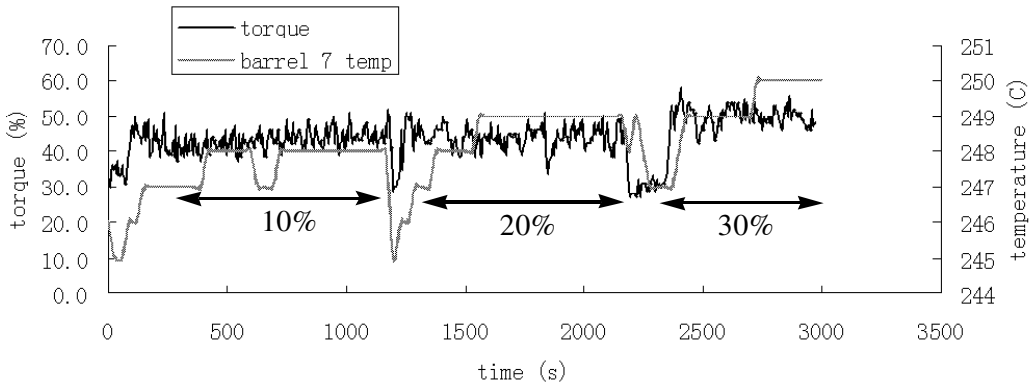

Figure 4.12 Torque and barrel 7 temperature of nylon 66/cellulose fiber during low temperature extrusion

Table 4.6 5% INTEC/nylon 66/cellulose fiber

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
245	250	255	230	230	230	230	200	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N66	CF
10%	256	262	253	249	252	49.8	120	11
20%	255	261	258	250	253	66.3	120	28
30%	253	261	263	250	253	71.0	100	44

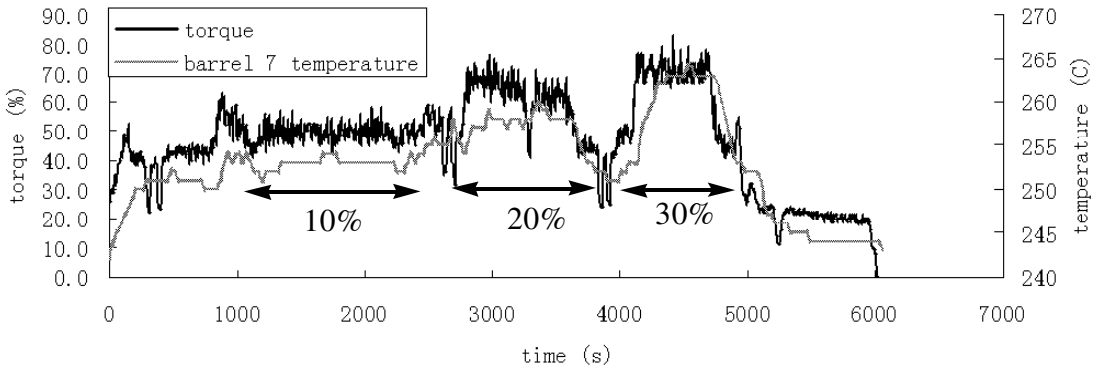

Figure 4.13 Torque and barrel 7 temperature of 5% INTEC/nylon 66/cellulose fiber during extrusion

Table 4.7 Plasticizer/nylon 66/cellulose fiber

Set Temperature (°C)							Screw Speed (rpm)	
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die		
230	240	240	230	230	230	230	250	
Actual Melt Temperature (°C)						Torque (%)	Feeding rate (g/min)	
	Barrel 2	Barrel 5	Barrel 7	Barrel 9	Die		N66	CF
10%	242	245	251	228	230	72.8	100	11
20%	244	246	254	229	231	69.8	85	20
30%	244	253	257	239	242	63.3	84	36

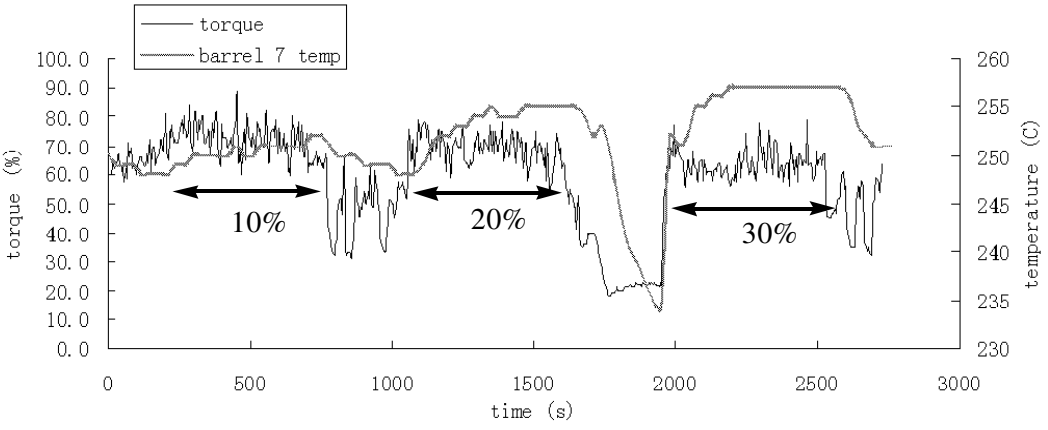

Figure 4.14 Torque and barrel 7 temperature of plasticizer/nylon 66/cellulose fiber extrusion

4.5 Optimization of extrusion parameters

From the analysis above we can see that the effects of processing parameters on the final properties are very complicated. To further understand how the set temperature, screw speed and feeding rate affect the thermal degradation of fiber, thus affect the final properties of composites, design of experiment will be used.

The initial purpose of this part is to study the effects of processing conditions on the final properties of nylon 6/cellulose fiber composites, and find the optimized processing parameters which lead to best mechanical properties.

4.5.1 Processing

The continuous extrusion - direct compression molding processing will be chosen to make cellulose fiber/nylon 6 composites. Matrix and cellulose fiber will be mixed by the twin screw extruder from NFM Welding Engineers, Inc. The extruder has seven heating zones. The nylon 6 is added in the first zone of the extruder with a screw feeder and the fibers from the 4^{th} zone with another screw feeder. The fiber content will be controlled by the feeding rate of the two feeders. Nylon 6 needs to be melted in zones 1-3. So the temperature of zones 1-3 are set to be 215, 220, 225 ^{o}C, above the melting temperature of nylon 6. The temperature of zones 4-7 can be lower, because nylon 6 needs a substantial amount of supercooling before it starts to freeze. The temperature profile of zones 4-7, screw speed and production rate will affect the properties of final products. The settings of these parameters are shown in the next section.

Hot mixture will be collected and compression molded directly to 12’×12’× 0.125’ square plaque while polymer is still melted. The plaque will be cut into 1’ ×5’

rectangles for flexural test, and into dog bones for tensile test. Tensile and flexural tests will be performed according to ASTM D 638 and ASTM D 790, respectively.

4.5.2 Modeling

4.5.2.1 Design of Experiment

To clearly understand the influence of extrusion processing parameters on the mechanical properties of composites, we'll run a 3^{3-1} experiment. To simplify the experiment, zones 4-7 are set to be the same temperature. The three factors are screw speed (A), production rate(B) and processing temperature of zones 4-7(C), the temperature of zones 1-3 is fixed to 215, 220, 225^{o} C. Each of the factors will be studied at three levels. The fiber content will be fixed to be 30% because the fibers in the 30% composites degrade the most. (We don't want to change fiber content because if we treat fiber content as a factor, we need to run 27 experiments). We also have two co-variances: fiber content and thickness of the samples. We want to get 30% fiber content, 0.125' thick samples, but we can't control the number accurately. However, we can measure accurately the fiber content and thickness of samples. These two factors may also affect the final properties. The processing parameters of the nine runs are shown in Table 4.8. According to the previous experiments, if the screw speed is high, we can lower the temperature of zone 4-6 more. So Factor C is set to be the sliding level, it will change with the change screw speed. For example, if the screw speed is level 0, 200rpm, the three levels of temperature (C | A0) is 210, 220, and 230^{o} C. If the screw speed is level 1, 275 rpm, the three levels of temperature (C | A1) is 200, 210, and 220^{o} C. The design matrix is shown in Table 4.9.

Table 4.8 Influence factors

Factors	Level 0	Level 1	Level 2
A: Screw Speed (rpm)	200	275	350
B: Feeding Rate (kg/hr)	9	12	15
C｜A0: Temperature (°C)	210	220	230
C｜A1: Temperature (°C)	200	210	220
C｜A2: Temperature (°C)	190	200	210

Table 4.9 Design matrix for the extrusion of cellulose fiber/nylon 6 composites

Run #	Screw Speed(A)	Feeding Rate(B)	Temp (C=AB)	Temp (C=AB)	Temp (C=AB)
1	0	0	0	0	0
2	0	1	1	0	0
3	0	2	2	0	0
4	1	0	0	1	0
5	1	1	0	2	0
6	1	2	0	0	0
7	2	0	0	0	2
8	2	1	0	0	0
9	2	2	0	0	1

4.5.2.2 Responses

Torque of the extruder during processing, actual melting temperature, color of the composites, tensile and flexural strength will be considered as responses. For each run we tested five tensile samples and five flexural samples. Each sample has a different

thickness. The torque shown in Table 4.10 is the average of 3 minutes for each run. Fiber contents were determined by the feeding rate of two feeders. For each run we calibrated the feeders once. However, we couldn't calibrate the feeders very accurately. For each run the fiber contents are slightly different. Fiber content is treated as covariance.

The composites from different runs have different color. The color indicates the thermal degradation of cellulose fiber. Figure 4.15 shows the different sample color of each run. The gray value indicates the darkness of the sample. The darker the sample is, the lower the gray value is.

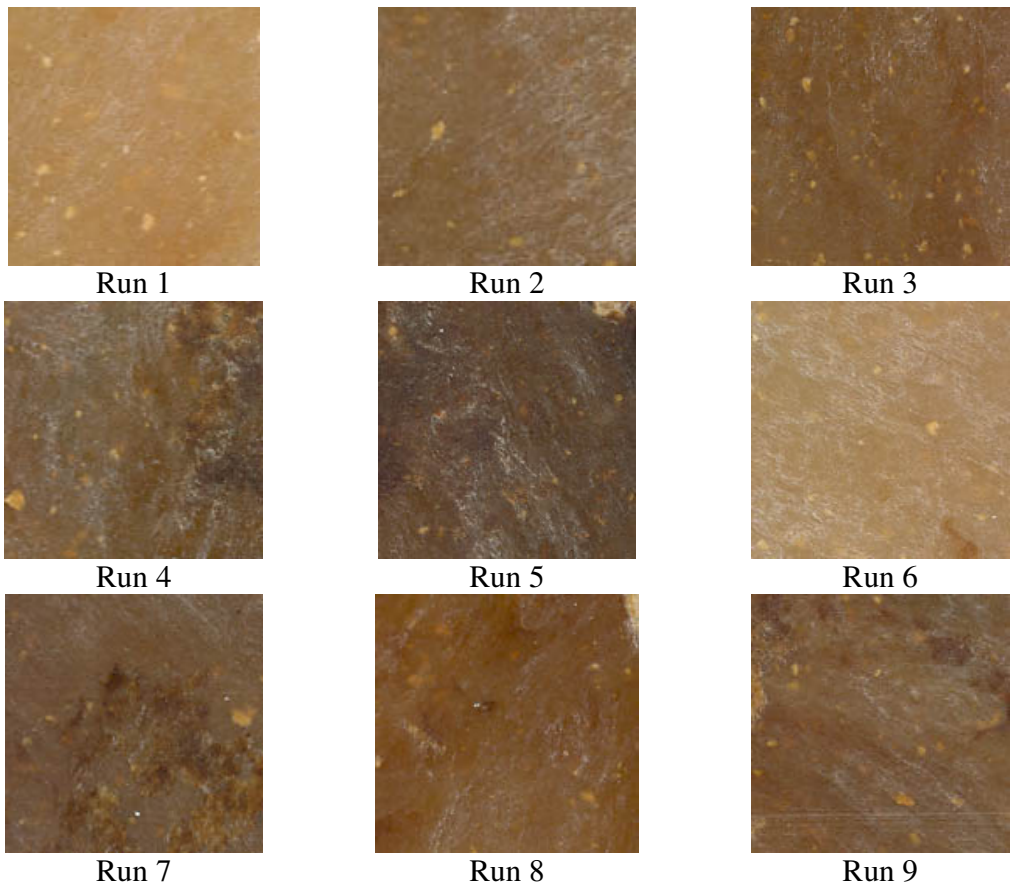

Figure 4.15 Sample color of run 1-9

Table 4.10 Responses of each run

Run #	Torque (%)	Gray Value	Fiber Content (%)
1	54.8	143	31.5
2	69.3	100	31.5
3	80.4	97.6	33.3
4	46.7	105	30.8
5	54.1	80	30.5
6	69.7	129	29.9
7	41.0	94	29.8
8	56.2	120	27.65
9	64.2	110	33.5

Run #	Barrel 5 Temperature (℃)	Barrel 7 Temperature (℃)	Barrel 9 Temperature (℃)	Actual Die Temperature (℃)
1	232	222	237	240
2	232	232	244	246
3	235	241	251	253
4	235	226	238	240
5	235	235	245	247
6	238	220	225	227
7	237	228	240	242
8	239	211	209	210
9	236	222	229	231

Table 4.10 Responses of each run (Continue)

Run #	Tensile Strength (MPa) (thickness (in))	S.D	Average
1	41.23(0.1339), 55.37(0.1330), 51.73(0.1226), 60.84(0.1358), 51.09(0.1384), 54.15(0.1395)	6.5	52.4
2	60.56(0.1495), 44.84(0.1488), 55.12(0.1468), 51.44(0.1471), 59.12(0.1470), 55.45(0.1441)	5.7	54.4
3	59.96(0.1616), 61.89(0.1600), 58.90(0.1613), 59.91(0.1635), 49.63(0.1644), 43.95(0.1648)	7.2	55.7
4	32.22(0.1235), 47.12(0.1224), 50.17(0.1211), 51.86(0.1239), 42.50(0.1243), 55.54(0.1218)	8.3	46.6
5	45.43(0.1395), 40.08(0.1358), 40.70(0.1390), 56.33(0.1404), 44.31(0.1400), 41.27(0.1425)	6.1	44.7
6	51.00(0.1560), 63.45(0.1555), 51.76(0.1561), 72.84(0.1550), 63.27(0.1538), 51.90(0.1489)	8.9	59.0
7	68.55(0.1305), 67.70(0.1290), 42.18(0.1308), 44.32(0.1306), 32.84(0.1304), 39.69(0.1318)	15.2	49.2
8	72.60(0.1234), 72.57(0.1259), 61.44(0.1274), 50.43(0.1284), 46.48(0.1334), 64.76(0.1219)	11.0	61.4
9	66.38(0.1848), 56.74(0.1883), 40.89(0.1799), 58.48(0.1909), 50.08(0.1913), 49.31(0.1815)	8.8	53.7

Run #	Flexural Strength (MPa) (thickness (in))	S.D	Average
1	96.482(0.1400), 98.704(0.1370), 104.538(0.1380), 112.537(0.1340), 104.660(0.1310)	6.3	103.4
2	112.224(0.1555), 111.470(0.1500), 114.494(0.1510), 114.191(0.1515), 120.094(0.1485)	3.4	114.5
3	107.737(0.1740), 111.003(0.1745), 111.154(0.1760), 122.493(0.1740), 110.512(0.1770)	5.7	112.6
4	100.359(0.1260), 9.180(0.1330), 75.305(0.1360), 95.675(0.1340), 66.330(0.1360)	14.2	85.4
5	87.579(0.1590), 85.613(0.1630), 74.316(0.1645), 84.531(0.1630), 80.044(0.1630)	5.3	82.4
6	99.953(0.1620), 102.922 (0.1690), 100.866(0.1650), 94.703(0.1680), 121.954(0.1680)	10.4	104.1
7	89.958 (0.1260), 97.810(0.1280), 94.843(0.1310), 78.171(0.1330), 84.166(0.1290),	8.0	89.0
8	87.771(0.1490), 81.555(0.1530), 75.370(0.1560), 79.912(0.1545), 93.009(0.1580)	6.9	83.5
9	106.454(0.1665), 77.776(0.1540), 95.119(0.1550), 98.519(0.1620), 85.861(0.1510)	11.2	92.7

4.5.3 Analysis

Now look at the tensile and flexural strength. During the tensile test, the sample will break at the regions of high fiber content. Tensile strength has very high standard deviation. But for flexural strength, since sample was broken in the middle, the standard deviation is small. The standard deviation of tensile strength can represent the fiber dispersion. We tried to use the step regression to get models of standard deviation of tensile strength(TS(SD)), flexural strength (FS), vs. screw speed (A), production rate(B) processing temperature(C), thickness (t) and fiber content. Let A, B, C to represent the linear effect, A^2, B^2, C^2 the quadratic effect, and $A^iB^jC^k$ the interaction between A, B, or C. Performing the stepwise regression with α =0.05, the outputs of stepwise regression are:

$$TS(SD)=3050238+0.34A^2C \qquad R^2=61.93\%$$

$$FS=211-0.00086AC+0.00105B^2C-648t \qquad R^2=59.08\%$$

We can see that the R^2 of the models are around 60%, which means the models are not very accurate.

But we can get pretty accurate models for torque , actual temperature of melting composites and gray value. The models are:

$$Torque(*100) = 4265+1.82BC-0.00024AC^2 \qquad R2=97.09\%$$

$$Die\ temperature = -942.72+10.12C-0.0215C^2+0.00004A^2 \qquad R^2=98.62\%$$

$$Barrel\ 7\ temperature = 40.24+0.861C+0.00001A^2B \qquad R^2=98.95\%$$

$$Gray\ value = 404.0-5.41C^2-0.305A \qquad R^2=83.23\%$$

From the above equations we can see that the torque will increase with the increase of feeding rate (B) and decrease of screw speed (A) and temperature (C). Barrel 7 temperature will increase with the increase of temperature (C), screw speed (A), and

feeding rate (*B*). The temperature (*C*) dominates the equation because of the larger coefficient. The gray value will decrease with the increase of temperature (*C*) and screw speed (*A*). In another words, the darkness of the composites will increase with the increase of temperature (*C*) and screw speed (*A*). Also the gray value is more sensitive to the change of temperature. All the results are consistent with the qualitative analysis before. The quantitative results gave us a chance to control the procedure more precisely. For example, with the equation of torque, we can estimate if the extrusion can run smoothly without exceeding the torque limitation.

4.6 Reference

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CHAPTER 5

THEORETICAL MODELS

5.1 Theories of Reinforcement

5.1.1 Rule of Mixture

For continuous fibers with uniaxial orientation, the rule of mixtures is commonly used to estimate the modulus and strength. In the fiber direction, assuming perfect bonding between fiber and matrix, the properties are:

$$E_L = E_f V_f + E_m V_m$$
$$\sigma_{Ltu} = \sigma_{fu} V_f + \sigma_m' V_m$$

Where E_L and σ_{Ltu} are the modulus and strength of composites in the fiber direction. E_m and E_f are the modulus of matrix and fiber. V_m and V_f are the volume fraction of matrix and fiber. σ_{fu} and σ_m' are the stress in fiber and matrix at fiber failure.

Compared to the continuous fiber-reinforced thermosetting resins or laminates, the modeling of discontinuous fiber reinforced composite materials is more complex. The continuous processing, such as extrusion or injection molding, will cause complicated fiber orientation and fiber length distribution. To evaluate the properties of these final products, we need to consider the effect of fiber length distribution and fiber orientation distribution.

5.1.2 The Critical Aspect Ratio

One of the earliest theories developed by Cox is based on a shear-lag mechanism observed in fibrous composites. According to Cox[1], in shear-lag analysis, the main

aspects of controlling the properties of composites are critical length of the fiber and interfacial shear strength between fiber and matrix. The critical length, l_c, is defined as

$$\frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau_y}$$

Where τ_y is the shear stress on the cylindrical fiber-matrix interface, d is the fiber diameter, σ_{fu} is the maximum allowable fiber stress.

The critical length of the fiber in composites is a parameter which determines the amount of stress transferred to the fiber. That is, if the length to diameter ratio is higher than the critical aspect ratio, composites show superior properties, while for a fiber whose aspect ratio is smaller than the critical aspect ratio, composites show weaker peoperties.

The critical fiber length is usually determined by experiments, such as the fiber fragmentation test [2, 3], pull-out [4, 5], microdebonding [6] and Raman spectroscopy [7,8].

Assuming the interface between fiber and matrix is perfect, and fiber and matrix remain elastic during testing, the Cox model used the classical shear lag theory to get the tensile stress distributions along the fiber length.[(2)]

$$\sigma_f = E_f \varepsilon_m \left[1 - \frac{\cosh\ \beta(\frac{1}{2}l - x)}{\cosh\ \frac{1}{2}\beta l} \right]$$

Thus the fiber strain is given by

$$\varepsilon_f = \varepsilon_m \left[1 - \frac{\cosh \beta(\frac{1}{2}l - x)}{\cosh \frac{1}{2}\beta l} \right]$$

And $\beta = \frac{2}{d}\left[\frac{E_m}{E_f(1+\nu_m)\ln(\pi/4V_f)^{1/2}}\right]^{1/2}$

Galiotis [7] defined the critical fiber length as the length of fiber required to reach 0.9 times the maximum fiber strain. The ratio of $\varepsilon_f / \varepsilon_m$ reaches the value of 0.9 at somewhere *x* along the fiber. Twice of *x* is the critical fiber length. Thus, the critical fiber length can be calculated by

$$l_c = 2.303d\left[\frac{E_f(1+\nu_m)}{E_m}\right]^{1/2}\left[\ln\left(\frac{\pi}{4V_f}\right)^{1/2}\right]^{1/2}$$

Where *d* is the fiber diameter, ν_m the Poisson's ratio of matrix, E_f and E_m the modulus of fiber and matrix, and V_f the volume fraction of fiber. The volume fraction is usually chosen to be 0.001 for single fiber composites.

5.1.3 Modulus

Many approaches have been proposed for prediction the elastic properties of composite materials incorporating discontinuous reinforcement such as short fibers. Very crude approximations to the composite modulus E_c are given by simple "law of mixtures' relationships in terms of matrix modulus (E_m), fiber modulus (E_f), and fiber volume fraction (V_f). Such equations, however, do not incorporate the influence of all structural parameters. Some investigators modified the 'rule of mixtures' by introducing parameters such as 'efficiency factors' to account for fiber aspect ratio and orientation distributions.[9] The relatively simple Cox-Krenchel model is a widely used one. [10]

$$E_c = K_\theta K_l E_f V_f + E_m V_m$$

Where K_θ, K_l denote the efficiency factors of fiber orientation and length.

$$K_l = 1 - \left(\tanh \frac{1}{2} \beta l \right) \Big/ \frac{1}{2} \beta l$$

$$\beta = \left(\frac{2G_m}{E_f r_f^2 \ln(R / r_f)} \right)^{\frac{1}{2}}$$

Where G_m is the shear modulus of the matrix, r_f and R denote the fiber radius and the interval among fibers. If the distribution of the fibers is homogeneous, distribution in an ideal packing square composite, R, is given by

$$R = \frac{r_f}{2} \sqrt{\frac{\pi}{V_f}}$$

If the reinforcing fiber length is variable with the distribution density h(l),

$$K_l = \frac{1}{\langle l \rangle} \int \left(1 - \frac{\tanh(\beta l / 2)}{\beta l / 2} \right) h(l) dl$$

K_θ is determined by the fiber orientation distribution. Neglecting transverse deformation, K_θ is 3/8 for random in-plane orientation of fiber, and 1/5 for random three dimensional fiber orientation.

The modulus calculated above is the tensile modulus. For flexural modulus, the compression ratio, K, needs to be added. [10]

$$E_c = K K_\theta K_l E_f V_f + E_m V_m$$

K was calculated by

$$K = \frac{W_f}{\rho_f} \Big/ \left[V - \left(\frac{W - W_f}{\rho_m} \right) \right] \text{v}$$

Where V, W, W_f, ρ_f, and ρ_m denote the volume of the original fiber and the composite specimen, the weight of the composite specimen and the fiber, and the density of the fiber and matrix, respectively.

The following equations are used to calculate the longitudinal and transverse modulus of oriented discontinuous fiber reinforced composites with the Halpin-Tsai model. [11]

Longitudinal modulus:

$$E_{11} = \frac{1 + \xi_{E_{11}} \eta_{E_{11}} V_f}{1 - \eta_{E_{11}} V_f} E_m$$

$$\xi_{E_{11}} = 2\left(\frac{\bar{l}}{d}\right) + 40V_f^{10}$$

$$\eta_{E_{11}} = \frac{E_{af} / E_m - 1}{E_{af} / E_m + \xi_{E_{11}}}$$

Transverse modulus:

$$E_{22} = \frac{1 + \xi_{E_{22}} \eta_{E_{22}} V_f}{1 - \eta_{E_{22}} V_f} E_m$$

$$\xi_{E_{22}} = 2 + 40V_f^{10} \text{ (10 is the power)}$$

$$\eta_{E_{22}} = \frac{E_{tf} / E_m - 1}{E_{tf} / E_m + \xi_{E_{22}}}$$

Where E_{11} and E_{22} are the longitudinal and transverse modulus of composite, E_m is the modulus for isotropic matrix, E_{af} and E_{tf} are the axial and transverse modulus of fiber. $\bar{l}$ is the average fiber length, d is the fiber diameter.

And for randomly oriented discontinuous fiber composites, the modulus is:

$$E_{random} = \frac{3}{8}E_{11} + \frac{5}{8}E_{22}$$

Many more complicated micromechanics models, such as Eshelby, Mori-Tanaka, vanished fiber, etc, need Poisson's ratio and shear properties of the fibers. Unfortunately, these properties of cellulose fiber haven't been exhaustively characterized. [23-25]

5.1.4 Tensile Strength

There are several models to estimate the elastic properties of composites. The models for strength of short fiber reinforced composites are still under development. Most of them are based on the rule of mixtures.

Bowyer and Bader [12] modified the rule of mixtures. Tensile strength is given by

$$\sigma_{cu} = K_1 K_2 V_f \sigma_{fu} + V_m \sigma_m'$$

Where K_1 and K_2 are, respectively, the fiber orientation and fiber length factors; σ_{cu} and σ_{fu} are the ultimate strength of the composite and fiber, respectively; V_f and V_m denote the volume fraction of the fiber and matrix; and σ_m' is the matrix stress at the failure of the composite. For unidirectional discontinuous composites $K_1=1$ and $K_2<1$.

If the fiber length is uniform and equals l, then

$$K_2 = l/(2l_c) \; for \; l < l_c$$
$$K_2 = 1 - l_c/(2l) \; for \; l \geq l_c$$

Where l_c, the critical fiber length, is given by $l_c = r_f \sigma_{cu} / \tau$, where τ and r_f are the interfacial shear stress between matrix and fibers and the fiber radius, respectively. Since fiber length will not be uniform after extrusion or injection molding, the rule of mixtures must be modified. Kelly and Tyson [2] then consider the effect of fiber length, longer and shorter than the critical fiber length. The modified model is given by

$$\sigma_{cu} = \sum_{l_i<l_c} V_i \sigma_{fu} l_i /(2l_c) + \sum_{l_j \geq l_c} V_j \sigma_{fu}[1 - l_c /(2l_j)] + V_m \sigma_m'$$

The first and second terms take into account the contributions of fibers with sub-critical length shorter than l_c and of fibers with super-critical length longer than l_c, respectively.

To consider the contribution of fiber orientation, the model is modified to:

$$\sigma_{cu} = K_1 \left\{ \sum_{l_i<l_c} V_i \sigma_{fu} l_i /(2l_c) + \sum_{l_j \geq l_c} V_j \sigma_{fu}[1 - l_c /(2l_j)] \right\} + V_m \sigma_m'$$

Many papers studied the probability density functions to model the fiber length and orientation distributions.[13,14]

For uniaxially oriented fibers K_1 is 1.0, while K_1 is 0.33 for random in-plane oriented fibers. This is the case most frequently encountered with our samples. For a thick part where random three-dimensional fiber orientation may occur, K_1 is 0.16. [15] Fukuda, et al gave the number to be 0.27. [16]

Z. Yu, etc [17] gave $K_1 = \left(\frac{2\langle P_2 \rangle_f + 1}{3} \right)^2$, where $<P_2>$ is related to the $cos^2\theta$. When fiber is oriented perfect along the flow direction, $<P_2>=1$, $K_1=1$. For random orientation, $<P_2>=0$, $K_1=1/9$.

5.2 Properties of Matrix and Fiber

5.2.1 Properties of Matrix

Table 5.1 Physical properties of nylon 6

	Density (g/cm^3)	Tensile Modulus (MPa)	Flexural Modulus (MPa)	Tensile Strength (MPa)
Nylon 6	1.13	1915	1365	44

5.2.2 Properties of Fiber

5.2.2.1 Estimation of modulus and strength

The mechanical properties of cellulose fiber haven't been characterized throughout. However, we can find the properties of natural fibers and wood pulps. The properties will be estimated according to the data available from natural fiber and wood pulp.

The 100% cellulose crystal elastic modulus in the chain direction was tested by X-ray, and the modulus is around 138Gpa. [18] For cellulose from woody plants, the degree of crystallinity is around 62-64%, [18] which means the modulus of our cellulose fiber should be lower than 138Gpa.

The highest tensile modulus and strength of natural fiber we can find is 128Gpa (Ramie) and 1000Mpa (soft wood kraft) [19], respectively. Since we can't find the information of cellulose fiber, we just use 128Gpa and 1000Mpa as the axial modulus and strength of cellulose fiber.

The transverse modulus, however, is more difficult to evaluate. Kevlar fiber has kind of similar structure with cellulose fiber. Both of them have hydrogen bond. Thus, we suppose they have similar transverse properties. The transverse modulus is 5Gpa, transverse strength is 7.9Mpa. [18]

Thus, the properties of cellulose fiber are:

Table 5.2 Mechanical properties of cellulose fiber

	Density (g/cm^3)	Longitudinal Modulus (GPa)	Transverse Modulus (GPa)	Longitudinal Strength (MPa)	Transverse Strength (MPa)
Cellulose fiber	1.5	128	5	1000	7.9

5.2.2.2 Effect of heat on properties

During processing, the fiber will be heated higher than its degradation temperature. The color of the composites is brown because of the thermal degradation of fibers. The heat history will definitely affect the properties of cellulose fiber. Since it's very difficult to do the single fiber tensile test, we converted cellulose fibers into hand sheets. The properties of the paper will be determined by the properties of cellulose fiber.

The paper will be aged at 220, 240, 260, 280℃ for 2 min. The color of the paper will be darker with the increase of temperature. We treat darkness as the sign of thermal degradation. Now we need to find the relationship between darkness and properties of the paper.

First the picture of aged paper was transferred to grey color (Figure 5-1). Then the data of each pixel on the paper were added to get the average value. This value shows the degree of darkness. Then modulus and strength of the paper were tested. The data are shown on Table 5.3.

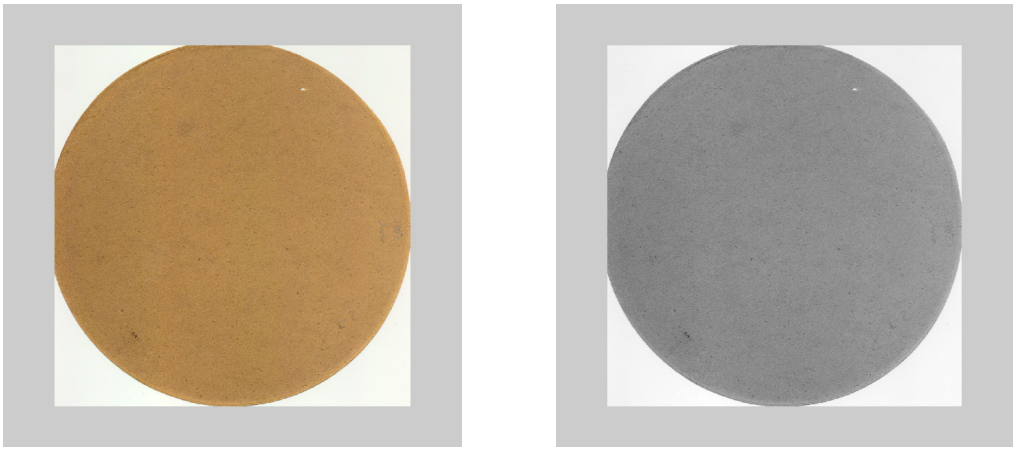

Figure 5.1 Transformation from RGB to Grey

Table 5.3 Modulus and strength vs. grey value

Aging temp (℃)	Grey Value	Modulus (MPa)	Max Load/width (N/mm)
220	252.75	132.5	0.801
240	234.9	125	0.776
260	194.2	82.9	0.579
280	140.9	74	0.445

At 220℃, the paper didn't get dark. We suppose the properties of paper didn't change at 220℃. The normalized modulus and strength vs. gray value are shown in Figure 5.2 and 5.3. We can see that at when gray value is between 140~260, modulus and strength are almost linear with gray value. After linear fitting, we get the relationships between normalized modulus and strength vs. gray value:

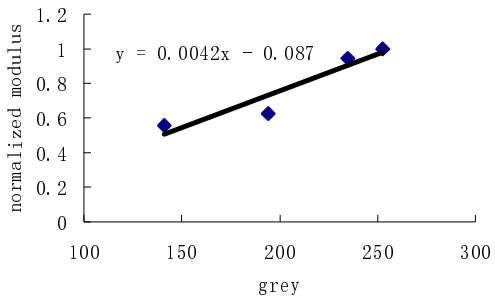

Figure 5.2 Normalized modulus vs. gray value

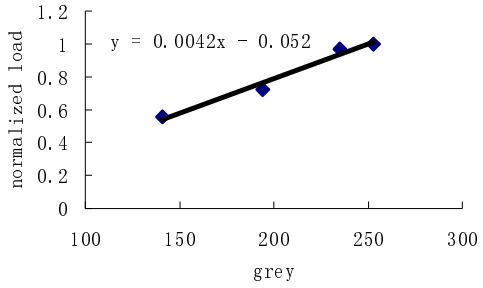

Figure 5.3 Normalized strength vs. gray value

Normalized modulus vs. gray value: *y=0.0042x-0.087*

Normalized strength vs. gray value: *y=0.0042-0.052*

If we assume the paper modulus and strength are linearly proportional with the modulus and strength of cellulose fiber, we can determine the final modulus and strength of cellulose fiber with thermal history with the above two equations.

Table 5.4 shows the gray value of extrusion-injection molded nylon 6/cellulose fiber composites and the calculated modulus and strength of the fibers.

Table 5.4 Final fiber strength and modulus after extrusion-injection molding

	Gray value	Normalized modulus	Normalized strength	Fiber modulus (Mpa)	Fiber strength (Mpa)
10% CF/N6	213	0.808	0.843	103	843
20% CF/N6	204	0.770	0.805	98.5	805
30% CF/N6	194	0.728	0.763	93.2	763

5.2.3 Critical Length

The critical fiber length is usually determined by experiments, such as fiber fragmentation test or pull-out. However, since our fiber is very short, it's not easy to do these tests. The interfacial shear strength of Ramie and epoxy is 16Mpa. [20] With the interfacial shear strength, fiber strength and diameter, we can calculate the critical fiber length by $\frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau_y}$.

5.3 Modeling Results and Analysis

5.3.1 Comparison between predicted properties and actual properties

Figure 5.4 shows the predicted tensile modulus with Halpin - Tsai model and Cox model. We can see that the Halpin -Tsai model gives very accurate prediction. But the Cox model doesn't work very well. One reason is that the Cox model didn't consider the anisotropic properties of the fiber.

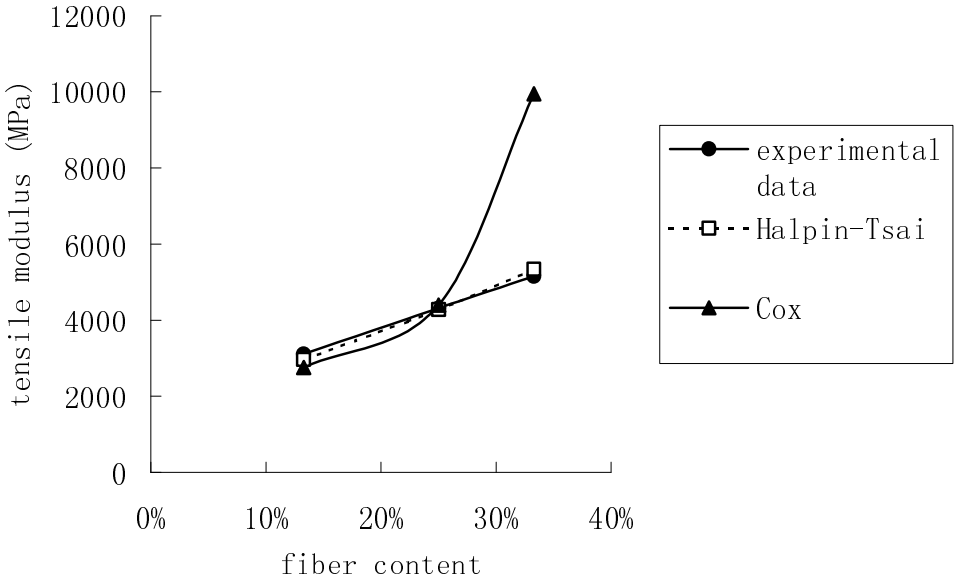

Figure 5.4 Comparison of predicted modulus and experimental result

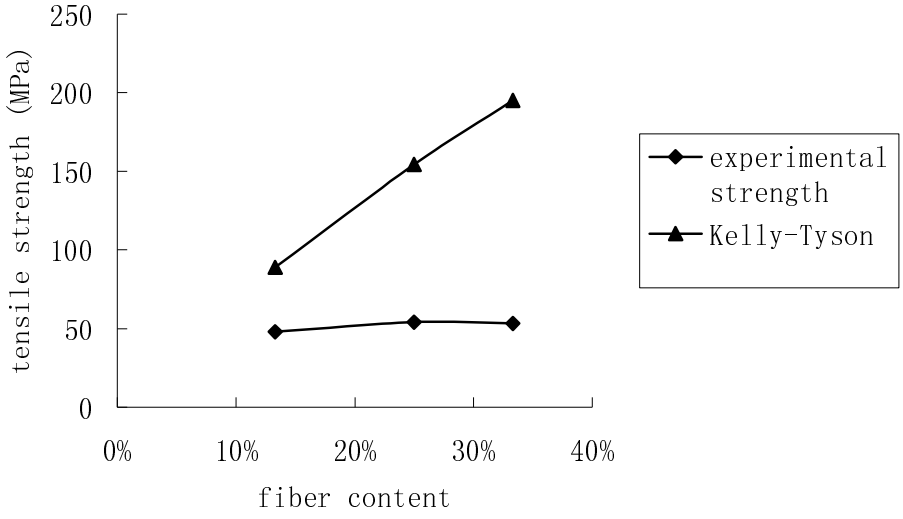

Figure 5.5 Comparison of predicted strength and experimental result

Figure 5.5 shows the predicted tensile strength with Kelly-Tyson model. We can see that the model didn't give good results. One possible reason is that the final fiber strength after thermal degradation wasn't estimated well.

It is reasonable to suppose fiber modulus is linearly proportional with the paper modulus. According to D. H. Page and R. S. Seth[21], the relationship between fiber modulus and paper modulus is

$$E_p = \frac{1}{3} E_f (1 - \frac{k}{R.B.A.})$$

where E_p is the paper modulus, E_f is the fiber modulus, k is a constant for a pulp sample, *R.B.A.* is the fraction of fiber surface bonded in the sheet.

From the above equation we can see that if k and R.B.A. remains constant or if R.B.A. is a large number, E_p is proportional to E_f.

However, it's not the right to assume the fiber strength is linearly proportional with the paper strength. The strength of paper is determined by both the strength of individual fibers and the bond strength between the fibers. D. H. Page gave a semi-empirical equation relating paper strength to a number of basic fiber and paper parameters. [22]

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bPL(R.B.A)}$$

where T is the tensile strength of paper, Z is the zero span tensile strength, indicates the fiber strength, A is the mean fiber cross sectional area, ρ is the density of the fibrous material, g is the acceleration due to gravity, b is the shear strength per unit area of the fiber-to-fiber bonds, P is the perimeter of the average fiber cross section, L is the mean fiber length, R.B.A is the fraction of fiber surface bonded in the sheet.

From the above equation we can see that during aging, the decrease of paper tensile strength (T) is not only related to the decrease of fiber strength (Z), but also the change of bonding strength (b). However, it's difficult to evaluate the effect of heat treatment on fiber strength and bonding strength separately.

5.3.2 Theoretical Analysis

The properties of the composites are determined by the fiber length, fiber properties and matrix properties. The theoretical properties with different fiber length or properties will tell how the factors affect the final properties. From the analysis in Chapter 4 we know that different processing parameters will cause different fiber length and fiber degradation. Understanding the effect of fiber length and properties on the composite properties will help us to determine the best processing parameters.

The properties of fiber will change by the heat treatment. The comparison between predicted and actual composite properties shows that the estimation of fiber modulus with different heat history is reasonable while the estimation of fiber strength is difficult. The Halpin-Tsai and Kelly-Tyson models will be used to simulate the composite properties with different fiber properties.

5.3.2.1 Effect of fiber properties

Fiber properties are the most important factors to determine the mechanical properties of composites. Fiber properties were affected by the thermal history during processing.

Figure 5.6 shows the effect of fiber modulus on the tensile modulus of composites. The matrix is nylon 6. Fiber length is fixed to be 0.283mm, the same as TC2500. The Halpin-Tsai model was used to predict the tensile modulus.

Three fiber moduli were chosen to be 128GPa, the same as TC2500 without thermal degradation, 64GPa and 32GPa. Figure 5.6 shows the estimated modulus. We can see that with the decrease of fiber modulus, the tensile modulus decreases. For 10% fiber content, the tensile modulus only decreases from 3.1GPa to 2.54GPa when fiber modulus decreases from 128GPa to 32GPa. With increase of fiber content, the tensile modulus is more sensitive to the fiber modulus. For 40% fiber content, composite tensile modulus decreases from 8.31GPa to 5GPa.

Figure 5.7 shows the effect of fiber strength and modulus on the tensile strength of composites. The matrix is nylon 6. Kelly-Tyson model was used to predict the tensile properties. Fiber length and modulus are set to be the same as TC2500.

From Figure 5.7 we can see that a decrease of modulus doesn't change the composite tensile strength a lot. The composite tensile strength with 500MPa fiber strength and 128GPa modulus is almost the same as strength with 500MPa fiber strength and 64GPa. The fiber strength dominates the composite tensile strength. When fiber strength decreases from 1000MPa to 500MPa, the composite tensile strength decreased almost half for all the fiber content.

This can explain why nylon 66 composites, especially high fiber content composites, have poor tensile strength but relatively high modulus. If the fiber was degraded severely, the modulus and strength all decreased a lot. The tensile modulus of composites is not sensitive with fiber modulus; while the tensile strength of composites will decrease proportionally with the decrease of fiber strength.

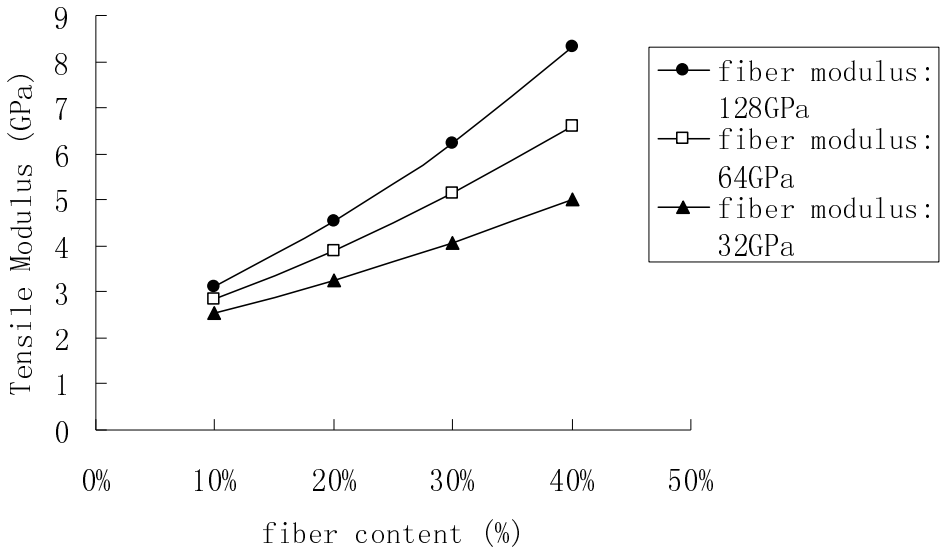

Figure 5.6 Effect of fiber modulus composite on tensile modulus of composites

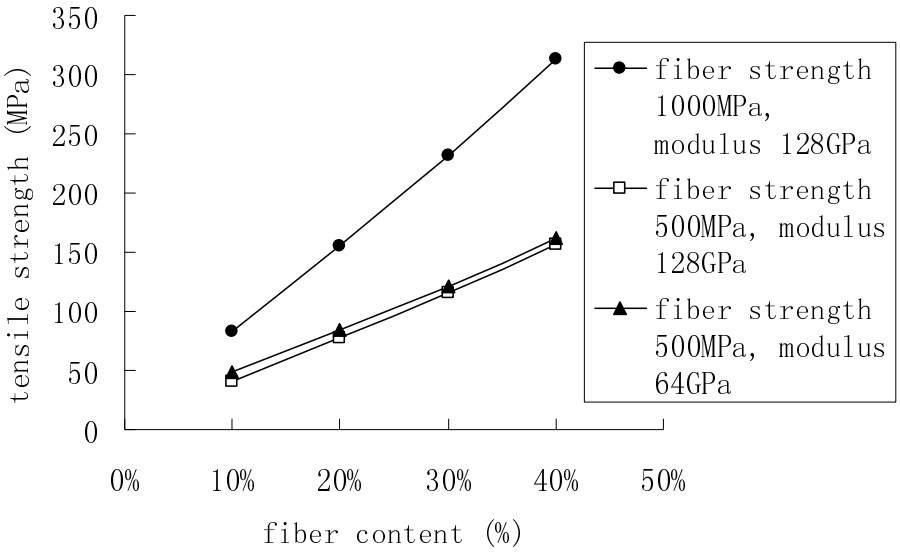

Figure 5.7 Effect of fiber strength on composite tensile strength

5.3.2.2 Effect of fiber length

Fiber length is another important factor that will affect the mechanical properties of composites. Fiber length will be affected by the processing. Table 3.15 showed the fiber length with different processing conditions. The shortened fiber length is 0.153mm, around half of the original fiber length.

Figure 5.8 shows the effect of fiber length on composite tensile modulus. The fiber modulus is set to be 128GPa, without thermal degradation. For 10% fiber content, when fiber length decreases from 0.283mm to 0.140mm, the tensile modulus decreases from 3.1GPa to 2.66GPa. For 40% fiber content, when fiber length decreases from 0.283mm to 0.140mm, the tensile modulus decreases from 8.3GPa to 6.1GPa.

Figure 5.9 shows the effect of fiber length on composite tensile strength. The fiber strength is set to be 1000MPa; and the fiber modulus is set to be 128GPa, without thermal degradation. We can see that the decrease of fiber length only decreases the composite

strength a little bit.

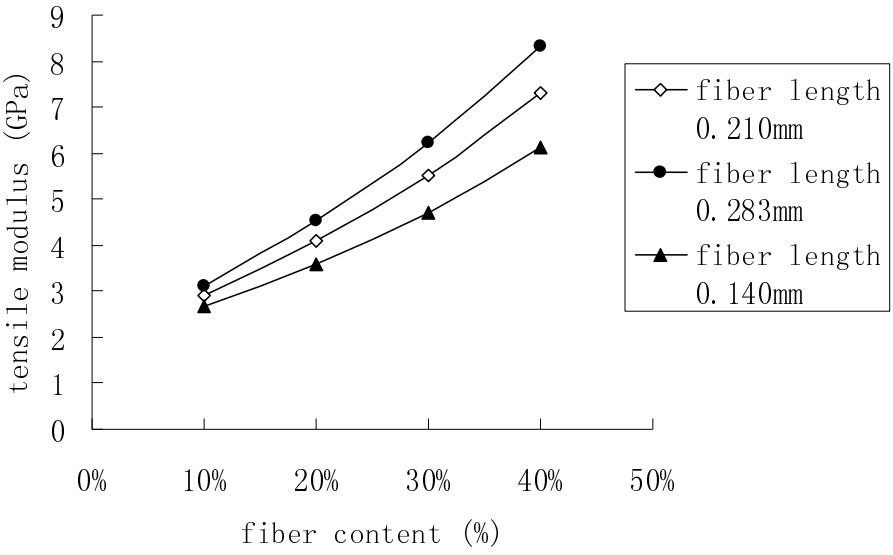

Figure 5.8 Effect of fiber length on composite modulus

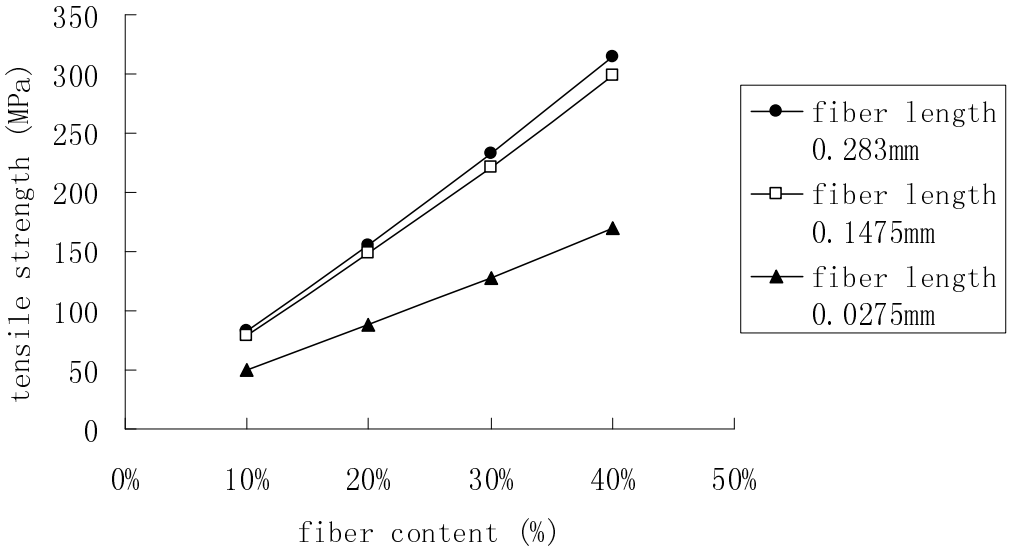

Figure 5.9 Effect of fiber length on tensile strength

This result indicates that increase the fiber strength is the key factor to increase the composite strength. During processing, the effect of processing parameters on fiber

length is not an important factor to be concerned. Fiber strength is the most important issue. If there is conflict between a decrease the fiber length and fiber strength degradation, choose the processing parameters that will decrease the thermal degradation of cellulose fiber, and thus increase the composite strength significantly.

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CHAPTER 6

WOOD/CELLULOSE FIBER REINFORCED RECYCLED POLYMER

6.1 Recycled Polypropylene/kenaf fiber

The 55% kenaf fiber reinforced polypropylene sheet is thermoformed for automotive applications. The trimmed waste needs to be recycled for both financial and environmental benefits. The content and density of each component of the recycled polypropylene/kenaf fiber is shown in Table 6.1.

Table 6.1 component content of recycled material

	Polypropylene	Kenaf fiber	PET
Content (%)	41.6	55	3.4
Density (g/cm^3)	0.907	1.5	1.37

The density of the recycled material was calculated to be 1.25 g/cm^3.

6.1.1 Compression Molding

6.1.1.1 Procedure

Coarsely ground recycled material was provided by Milliken Automotive. First this material was compression molded to 30.48 × 30.48 × 0.3175cm samples with Wabash compression molding machine. The size of the mold cavity was 30.48 × 30.48cm. To make sure the thickness of the sample was 0.3175cm, the volume of the compressed

panel was calculated to be 295 cm^3, and according to the density of the material, we can calculate the weight of the compressed panel to be 370g.

370g recycled material was weighed and put in the mold. The mold was put into the preheated Wabash machine with vacuum under minimum pressure. After a specific time the mold was cooled under set pressure. The heating temperature, time and pressure during cooling are shown in Table 6.2. Because of the high fiber content, CM#1, CM#2 and CM#3 all showed incomplete consolidation in the four corners. Figure 6.1 shows a quarter cut from CM#3 sample. It's clear that the upper right didn't get consolidated well. Only polymer in the middle of the plaque consolidated. CM#4 was compressed under high temperature and pressure. Most polymer consolidated.

Table 6.2 Compression condition and results

	Temperature (℃)	Heating Time (min)	Pressure (kpa)	Result
CM#1	199	30	654	No melt in four corners
CM#2	204	40	654	No melt in four corners
CM#3	210	45	654	No melt in four corners
CM#4	216	45	763	Better, choose middle part to test

Figure 6.1 Quarter of the CM#3 sample

The material contains 55% kenaf fiber. 27.3% recycled polypropylene from Eleison Composites, LLC was added to make 40% kenaf fiber content composites. 270g recycled kenaf/PP and 75g recycled PP was mixed and put into the 30 x 30cm mold. The weight of the materials makes sure the thickness of the plaque to be 0.3175cm. Because of the higher polymer content, the temperature for consolidation is 204℃, heating time 45min, pressure during cooling is 763kPa.

6.1.1.2 Mechanical test

Tensile test samples were prepared according to ASTM D638, type 1. The compression molded plaque was first cut to 16.5 x 1.9cm rectangular bar then milled into a dog bone shape using a Tensikut mill machine. All the tensile tests were conducted at

room temperature with an Instron 4466 universal test machine. The crosshead speed was 0.508cm/min. The detailed procedure in ASTM D638 was followed.

Flexural testing was performed according to ASTM D 790. The compression molded plaque was cut into 2.54 x 12.7cm rectangular samples. The samples were tested at room temperature on an Instron 4466 machine. The span length between two supporting noses was 5.08cm and the crosshead speed was 1.35cm/min. .

6.1.1.3 Mechanical properties

Tables 6.3 and 6.4 show the tensile and flexural properties and standard deviation (SD) of CM#4 and the 40% kenaf fiber/PP. 40% kenaf / PP has lower tensile and flexural modulus compared with 55% kenaf / PP composites. But 40% kenaf / PP has higher tensile and flexural strength than 55% kenaf / PP composites. One possible reason is that 40% kenaf / PP composites used lower temperature during compression molding. Thus 40% kenaf / PP had less thermal degradation than 55% composites. Also 40% fiber content composite has higher strain than 55% fiber content composite, as expected.

Table 6.3 Mechanical properties of CM#4 (55% kenaf/PP by CM)

	Modulus (GPa)	**Strength (MPa)**	**Strain (%)**
Tensile Mean	5.1	29	0.75
Tensile SD	0.32	3.5	0.15
Flexural Mean	5.1	57	1.64
Flexural SD	1.1	7.6	0.13

Table 6.4 Mechanical properties of 40% kenaf fiber/PP by CM

	Modulus (GPa)	Strength (MPa)	Strain (%)
Tensile Mean	4.3	31.6	1.1
Tensile SD	0.35	3.6	0.18
Flexural Mean	4.1	64.9	2.7
Flexural SD	0.22	2.09	0.12

6.1.2 Extrusion-Compression Molding

6.1.2.1 Procedure

The recycled material is shredded and has low density. It's not easy to feed the fluffy material with the normal feeder. The recycled material was converted to pellets for easier handling. The material was put into the30 x 30cm mold and consolidated. The mold was first heated to 210℃ for 20 minutes with vacuum, then cooled under 1090 kPa pressure. The plaque obtained from compression molding was then ground to small pellets with the SK-15 grinder from IMC Company. The pellets were then fed in the twin screw extruder for further processing.

The twin screw extruder includes six separately heating zones and a die (Figure 6.2). Material can be fed from feeder 1 or feeder 2. The hot mixture from the die is collected for one minute and compression molded directly to a plaque while the polymer is still melted. During compression molding, 0.3175cm thick sheet is put between the top and bottom molds to control the plaque thickness. The plaque was cut into samples for flexural and tensile testing.

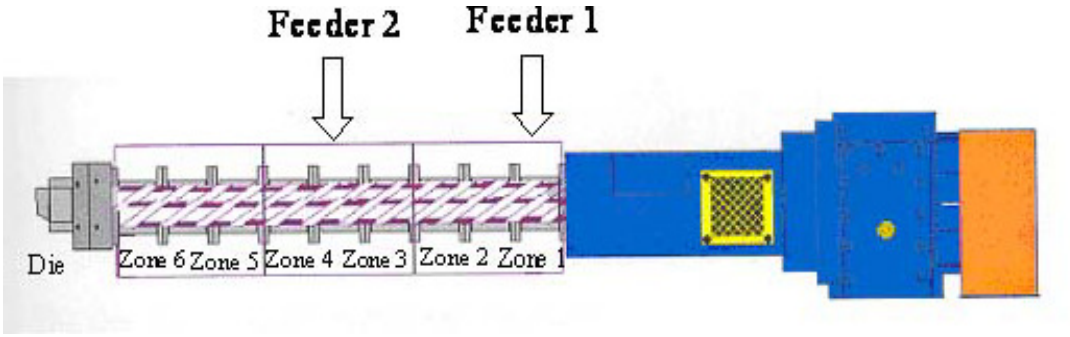

Figure 6.2 Schematic figure for twin screw extruder

6.1.2.2 Normal processing temperature

The temperature profile of sample EX#1 and EX#2 is shown in Table 6.5. For EX#1, the 55% kenaf/PP was fed from feeder 2 for shorter thermal history. Nothing was fed from feeder 1. For EX#2, the recycled PP powder was fed from feeder 1, 55% kenaf/PP was fed from feeder 2. Recycled PP and 55% kenaf/PP was fed by ratio to make sure 40% kenaf/PP was obtained at the die. EX#1 is 55% kenaf/PP composite, and EX#2 is 40% kenaf/PP composite.

Table 6.5 Extrusion temperature profile for EX#1 and EX#2

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
160	170	180	190	190	190	190

The mechanical properties of EX#1 and EX#2 are shown in Tables 6.6 and 6.7. It is clear that similar with compression molded samples, 40% fiber content composite has lower modulus, higher strength, and higher strain. But compared with compression molded samples, the extrusion-compression molded samples have lower modulus and strength. The reason is that during collecting the hot melt from the die with a metal plate,

the melted polymer tends to solidify. Before compression, part of the polymer has already solidified, thus causing more voids and defects.

Table 6.6 Mechanical properties of EX#1 (55% kenaf/PP by EX/CM)

	Modulus (GPa)	Strength (MPa)	Strain (%)
Tensile Mean	3.6	20	1.13
Tensile SD	0.57	2.3	0.32
Flexural Mean	2.9	36	2.65
Flexural SD	0.67	12	0.56

Table 6.7 Mechanical properties of EX#2 (40% kenaf fiber/PP by EX/CM)

	Modulus (GPa)	Strength (MPa)	Strain (%)
Tensile Mean	3.4	26.9	1.5
Tensile SD	0.33	4.5	0.49
Flexural Mean	1.5	37.5	4.42
Flexural SD	0.25	7.5	0.50

6.1.2.3 Lower processing temperature

During extrusion we also found that the processing can be done under lower temperature. The temperature of each heating zone was dropped 10^{o} C. Table 6.8 shows the temperature profile of sample EX#3 and EX#4. For EX#3, the 55% kenaf/PP was fed from feeder 2 only. EX#3 contains 55% kenaf fiber. For EX#4, the recycled PP powder was fed from feeder 1, 55% kenaf/PP was fed from feeder 2. EX#4 contains 40% kenaf fiber.

Table 6.8 Extrusion temperature profile for EX#3 and EX#4

Temperature (^{o}C)						
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die
150	160	170	180	180	180	180

Table 6.9 Mechanical properties of EX#3 at lower temperature

(55% kenaf/PP by EX/CM)

	Modulus (GPa)	**Strength (MPa)**	**Strain (%)**
Tensile Mean	3.7	36	2.1
Tensile SD	0.21	1.2	0.12
Flexural Mean	2.8	58	4.11
Flexural SD	0.21	3.6	0.31

Table 6.10 Mechanical properties of EX#4 at lower temperature

(40% kenaf fiber/PP by EX/CM)

	Modulus (GPa)	**Strength (MPa)**	**Strain (%)**
Tensile Mean	3.1	28	1.6
Tensile SD	0.67	2.4	0.5
Flexural Mean	1.7	46	4.9
Flexural SD	0.45	6.2	0.89

Table 6.9 and 6.10 show the mechanical properties of EX#3 and EX#4. We can see that with lower extrusion temperature, the modulus and strength of both samples are higher than the high extrusion temperature samples. This indicates that the processing temperature is still an essential issue for the properties of natural fiber reinforced polypropylene. It is possible to decrease the extrusion temperature more with the so called 'Low temperature compounding' technique. More research can be done here.

6.1.3 Extrusion-Injection Molding

Composites coming from the extruder were collected and ground to small pieces by the IMC grinder. The small pieces were then injection molded into tensile and flexural test samples. The EX#3 samples were collected and injection molded. The injection molding conditions are shown in Table 6.11.

Table 6.11 Injection Molding temperature profile for EX#3

(55% kenaf/PP by low temperature extrusion)

Temperature (^{o}C)					
Zone 1	Zone 2	Zone 4	Zone 5	Zone 6	Mold
170	180	190	190	190	27

The mechanical properties of extrusion-injection molding samples are shown in Table 6.12. It is clear that extrusion-injection molded samples have much higher modulus than compression or extrusion-compression samples. This can be explained by the lower void content of injection molded samples. But the strength is lower, this is because after compression-extrusion-injection molding, the samples experience more thermal history than simply compression or extrusion-compression.

Table 6.12 Mechanical properties of extrusion-injection molded samples

(55% kenaf/PP by EX/IM)

	Modulus (GPa)	Strength (MPa)	Strain (%)
Tensile Mean	6.2	31	0.83
Tensile SD	0.35	2.9	0.13
Flexural Mean	4.8	48	1.75
Flexural SD	0.33	6.8	0.29

6.1.4 Density analysis

Table 6.13 Densities of kenaf/polypropylene composites

Sample #	Procedure	Density (g/cm^3)
CM#3	Unsolidified upper right	0.869
CM#4	Solidified CM	1.11
EX#1	55%, EX-CM	1.103
EX#2	40%, EX-CM	1.017
EX#3	55% EX-CM, Low Temp	1.028
EX#4	40% EX-CM, Low Temp	1.035
EX-IM	55% EX-IM	1.145

Table 6.13 shows the densities of the kenaf/polypropylene composites from different processing methods. The unsolidified compression molded sample has very low density. It's lighter than water. The solidified compression molded sample has relatively higher density, but still lower than the theoretical density, $1.25 g/cm^3$. Extrusion-compression molded samples are a little bit lighter than solidified compression molded composites.

The extrusion-injection molded sample has the highest density in all the composites. This means the injection molding gave the samples with less voids.

6.1.5 Comparison to reported properties of wood/polypropylene composites

Kenaf is a strong natural fiber with long length. [1] But the fiber was chopped to short length during grinding. The properties of kenaf/polypropylene composites made from Milliken recycled material should be comparable with wood flour/polypropylene composites.

There are a lot of reports related to wood flour/polypropylene composites. [2-5] Table 6.14 shows the wood/polypropylene composite properties produced by North Wood Plastics, Inc.[5] The properties of injection molded kenaf/PP are comparable with 60% wood/PP composites.

Table 6.14 Mechanical properties of commercialized wood/polypropylene composites [5]

	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)
60% wood/PP, Extrusion Grade	21	6	42	4.9
60% wood/PP, Molding Grade	20	6.2	39	4.2
40% wood/PP, Extrusion Grade	31	3.9	54	3.9
40% wood/PP, Molding Grade	25	3.3	48	3.3

6.1.6 Summary and suggestions

Compression, extrusion-compression and extrusion-injection molding were used to recycle the 55% kenaf/polypropylene composites. For compression, because of high fiber content, the composite is difficult to consolidate. The composite needs a high temperature

and a long heating time to consolidate, which causes thermal degradation of kenaf fiber. To extrude the composite, the fluffy material needed to be converted to small pellets for better feeding. The composites were first compressed then extruded. The compression procedure adds thermal history to the kenaf fiber. Extrusion-compression molding procedure gives product with high void content. Extrusion-injection molding procedure gives product with low void content but injection molding reheated the material and increased the thermal degradation of the kenaf fiber. Each method has advantages and disadvantages. Extrusion-injection molding gives the best modulus while low temperature extrusion-compression molding gives the best strength.

The NGR from Next Generation Recycling Maschinen GmbH is a single screw extruder with a shredder incorporated in the feed section. The recycled composite can be fed to the shredder by crammers and blown into the extruder barrel. Without the compression-grinding to pellets procedure, the NGR can convert the material to pellets directly. The pellets then can be injection molded to samples. Or the hot mixture from the NGR can be compression molded directly into samples. The parameters of extrusion and injection molding, especially the temperature profiles, will affect the properties of the final product significantly. During the former study we found that the processing temperature can be lower than the recommended processing temperature of polypropylene for decreasing the thermal degradation. Feeding rate can change the time of the material stays in the extruder, and thus affect the thermal history. Screw speed can affect the thermal history, it can also affect the shear rate, and thus affect the fiber length, which is also an essential issue for the final properties. The optimization of processing parameters can be achieved through more research.

6.2 Recycled carpet

In 2003, 4,828 million of pounds carpet was discarded with only 1.8% being recycled [6]. By 2012, 6,772 million pounds of carpet will be discarded. [6] In January 2002, carpet and fiber manufacturers signed the National Carpet Recycling Agreement, Memorandum of Understanding for Carpet Stewardship (MOU). This agreement established national goals for the years 2002-2012 to increase the amount of recycled carpet and reduce the amount of waste carpet going to landfills. [6]

Figure 6.3 shows the structure of tufted carpet. [7] It contains around 50% face fiber, mainly made from nylon 6, nylon 66, polypropylene, acrylic, polyester, wool or cotton; 15% backing fabric, mainly made from polypropylene, and 35% adhesive, mainly made of styrene butadiene latex rubber (SBR) and $CaCO_3$. [8] In these components nylon 6 and nylon 66 are high value engineering thermoplastics. So recycled carpet is a good resource of nylon 6 and nylon 66.

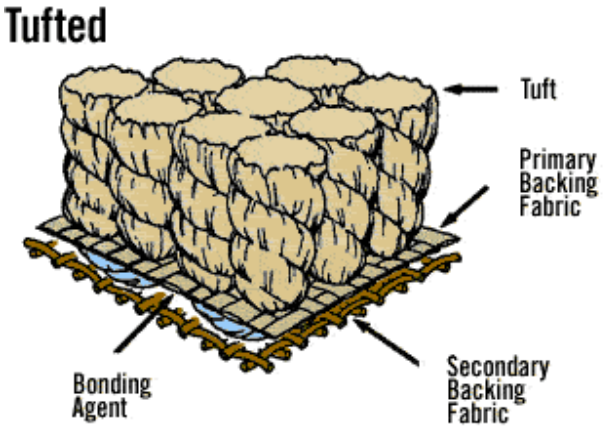

Figure 6.3 Tuft carpet structure [7]

First, the post consumer carpet is sorted by face fiber using a near infrared(NIR) sensor to identify the face fiber. Then the sorted carpet was shredded and pelletized by a

NGR A- Class Type 55 Repelletizing System. Figure 6.4 shows a schematic of the NGR system. The cutter can chop the carpet to small pieces then feed the pieces to the screw.

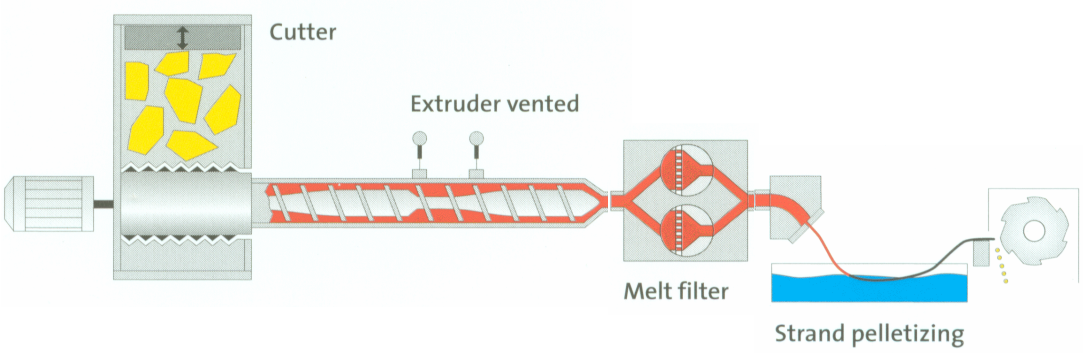

Figure 6.4 Schematic figure of NGR A- Class Type 55 Repelletizing System

Recycled carpet is a good resource of nylon 6 or nylon 66. It's possible to make low cost, high performance cellulose fiber reinforced recycled nylon 6 or 66 composites. According to the experiments and analysis in chapter 3 and 4, I recommend to use 3% INTEC/recycled nylon 6 and 3% INTEC/3% LiCl/nylon 66 as matrix.

6.3 References

(1) D. Puglia, J. Biagiotti and J. M. Kenny, *Polymer Analysis, Degradation, and Stabilization*, Nova Science Publishers, Inc. 95-140, (2005)

(2) N. M. Stark and R. E. Rowland, *Wood and Fiber Science*, 35(2), 167-174, 2003

(3) M. N. Ichazo, C. Albano, J. Gonzales, R. Perera, and M. V. Candal, *Composites Structures*, 54, 207-214 (2001)

(4) Q. Lin, X. Zhou, G. Dai and Y. Bi, *Journal of Applied Polymer Science*, 85, 536-544 (2002)

(5) D. O. Kipp, Plastic Material Data Sheets, MatWeb - Division of Automation Creation, Inc. (2004)

(6) *CARE (Carpet America Recovery Effort)* 2003 Annual Report

(7) http://www.carpet-rug.org/commercial-customers/selecting-the-right-carpet/carpet-and-rug-construction.cfm, June 2008

(8) *Carpet Primer 2002*. www. Carpet-rug.com, May 2004

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The key conclusions of this study are:

1. For cellulose fiber/nylon 6 composites, extrusion-injection molding gave better mechanical properties than extrusion-compression molding. Low temperature extrusion gave better properties than high temperature extrusion. 3% INTEC/nylon 6 matrix gave best properties because it can decrease the processing temperature and cooling time during injection molding. Modulus and strength increase with the increase of fiber content. For 30% cellulose fiber, the tensile modulus of the composite can reach 5GPa; the tensile strength is 68MPa; the flexural modulus is 4GPa, and the flexural strength is 100MPa.
2. For cellulose fiber/nylon 66 composites, extrusion-injection molding gave better mechanical properties than extrusion-compression molding. Low temperature processing gave better properties than high temperature. 3% INTEC/3% LiCl/3% NBBSA/nylon 66 matrix gave best properties because it can decrease the processing temperature and cooling time during injection molding. Modulus increases with increasing fiber content. Strength decreases with increasing fiber content, which indicates the fiber degradation is still severe. For 30% fiber content, the tensile modulus can reach 5GPa; the tensile strength is 50MPa; the flexural modulus is 5GPa; and the flexural strength is 90MPa. For 10% fiber content, the tensile strength is 70MPa; the flexural

strength is 147MPa; the tensile modulus 4GPa; and the flexural modulus 3.7GPa.

3. The actual melt temperature in the barrel may be different than the set temperature. Viscous heating causes the increase of melt temperature. With increasing fiber content, viscosity increases, thus causing an increase in melt temperature. This explains why there is more thermal degradation of 30% cellulose fiber composites at the same processing parameters compared to lower fiber percentages. Screw speed, feeding rate and set temperature can affect the mechanical properties of composites by affecting thermal degradation, fiber length distribution, and fiber dispersion.
4. Theoretical modeling shows that the change of fiber properties determines the final properties of composites. Fiber length has minor affect on both modulus and strength as long as the fiber length is above the critical length. If there is a conflict between decreased fiber length and fiber strength degradation, choose the processing parameters that will decrease the thermal degradation of cellulose fiber.

6.2 Recommendations

The following suggestions are recommended for further study:

1. The torque limitation limits the extrusion of composites. Feeding rate has to be reduced; temperature can't decrease to the lowest limit; NBBSA has to be added to LiCl/nylon matrix to decrease the viscosity. An extruder with higher power can be used to solve these problems.

2. Compression molding gave lower mechanical properties than injection molding even though the thermal degradation of fiber is lower than injection molding. One reason is that fiber didn't disperse well in matrix. Analysis shows fiber length isn't an important factor for mechanical properties. Increasing screw speed can be tried to see if fiber dispersion is improved even if it can decrease fiber length.
3. During extrusion-compression molding processing, the hot mixture was collected with a metal plaque. During collection the polymer gets consolidated. The samples from compression molding have higher void contents. If the metal plaque was heated above the melting temperature of polymer during collection, the void content may be decreased.
4. Recycled carpet is a good resource for nylon 6 and nylon 66. Cellulose fiber can be used to reinforce nylon 6 or nylon 66 from recycled carpet to make low cost, high performance composites.
5. The estimation of fiber strength with thermal degradation is not accurate, thus the modeling of composite strength is not accurate. More study needs to be done to find the affect of thermal degradation on fiber strength.

APPENDIX A

DSC OF PLASTICIZER/NYLON 6 OR NYLON 66

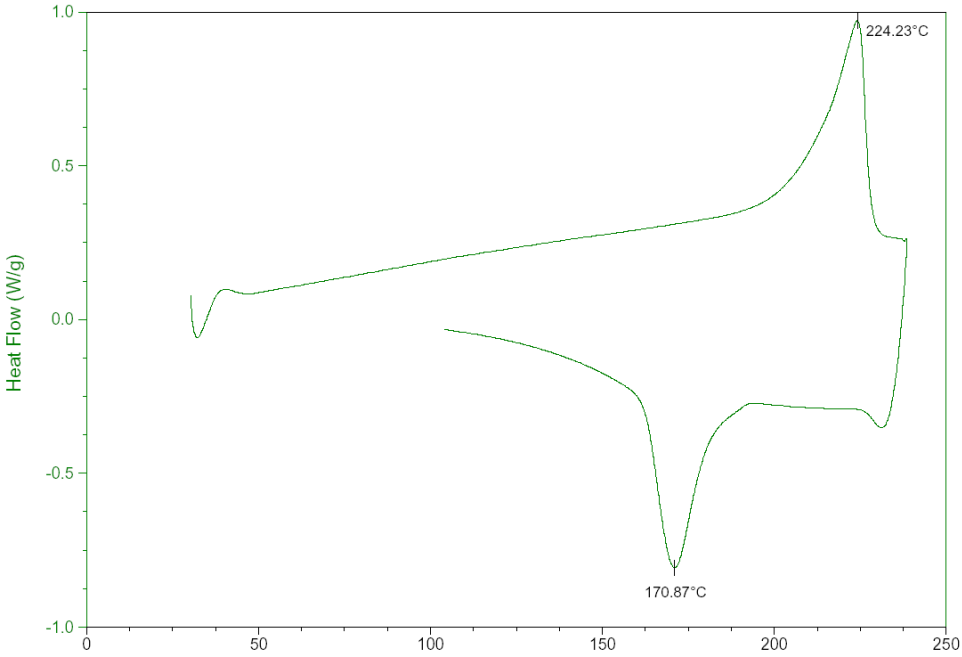

Figure A.1 DSC of nylon 6

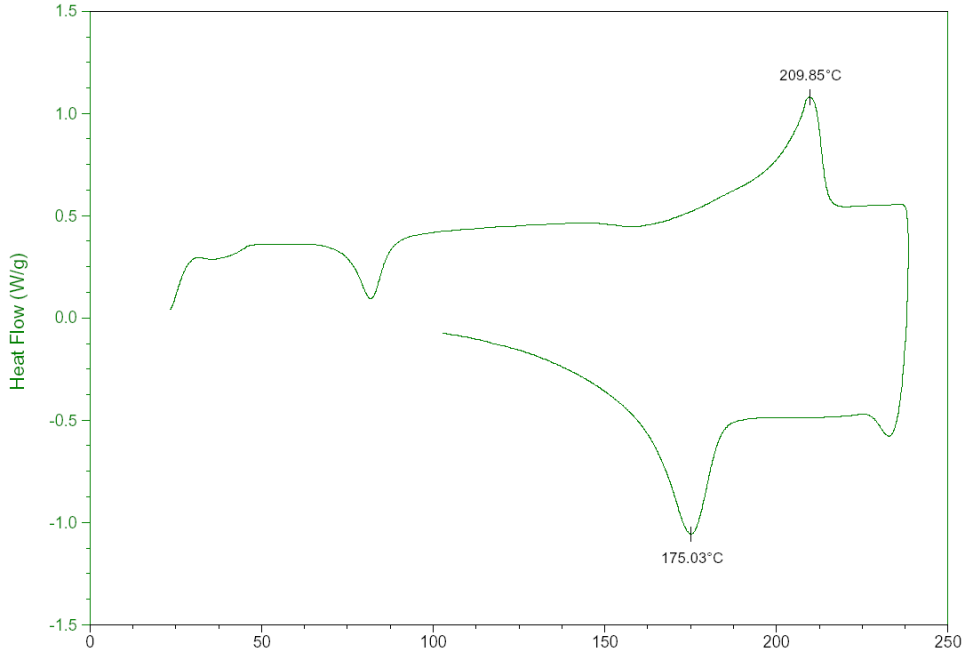

Figure A.2 DSC of 3% LiCl/Nylon 6

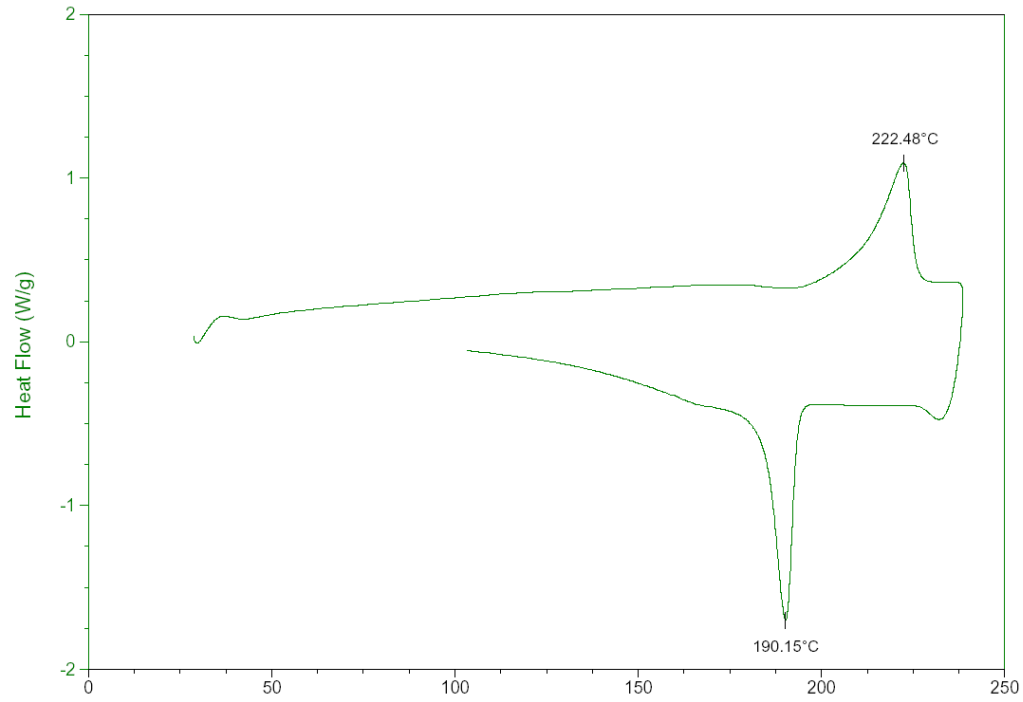

Figure A.3 DSC of 3% NBBSA/nylon 6

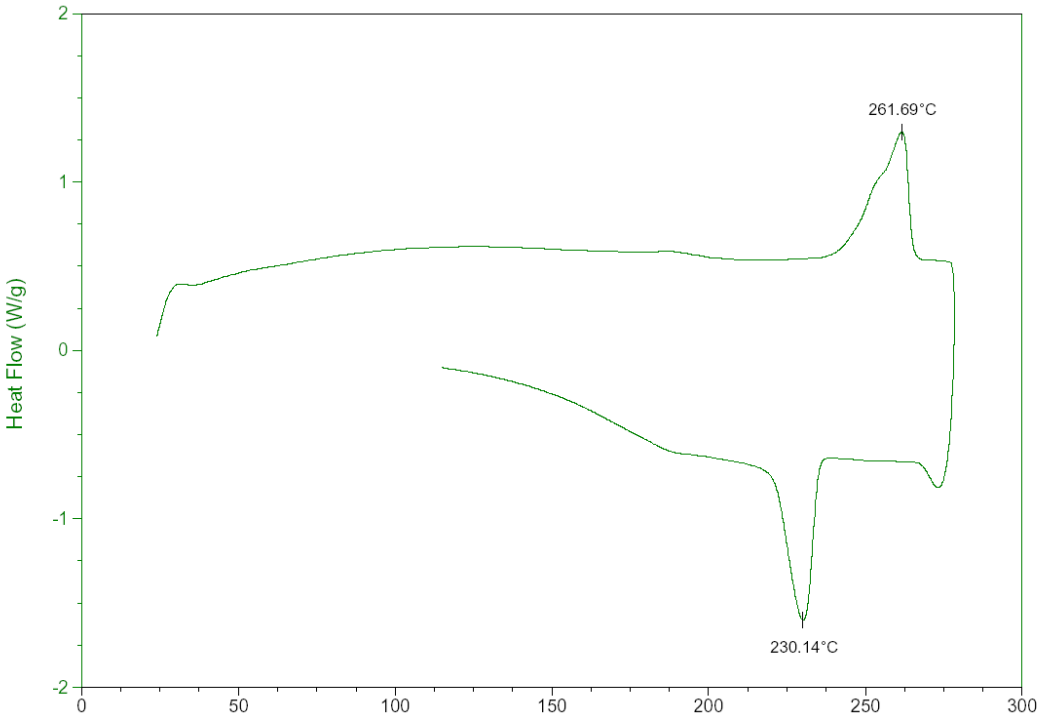

Figure A.4 DSC of nylon66

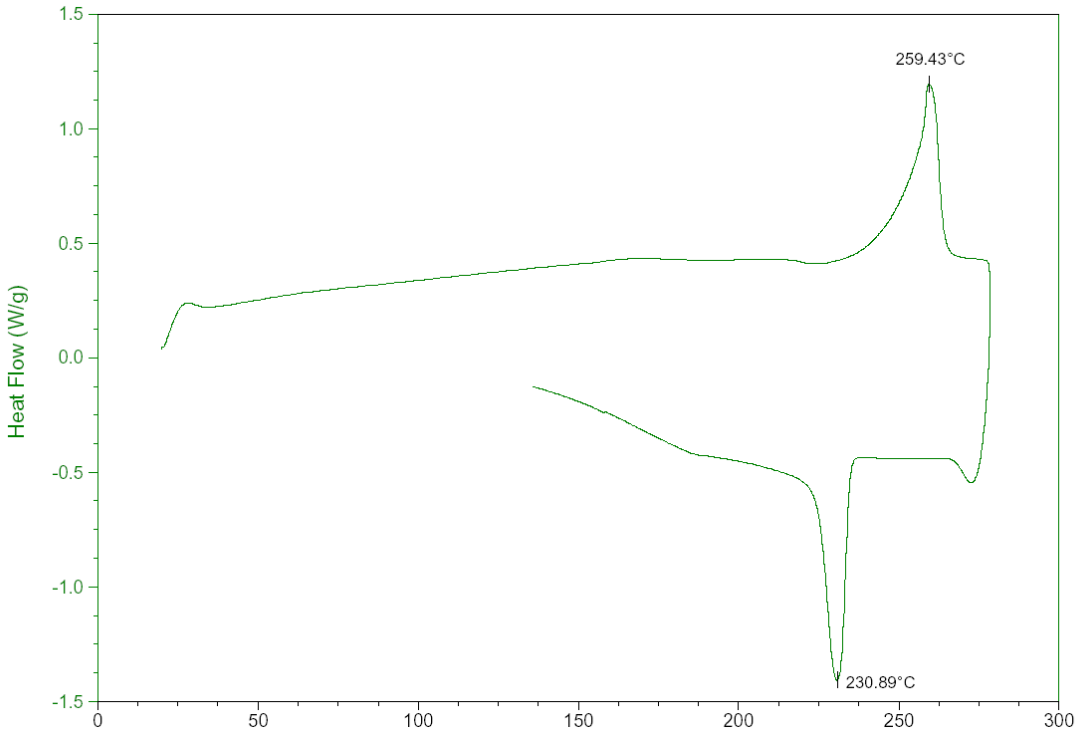

Figure A.5 DSC of 10% caprolactam/nylon 66

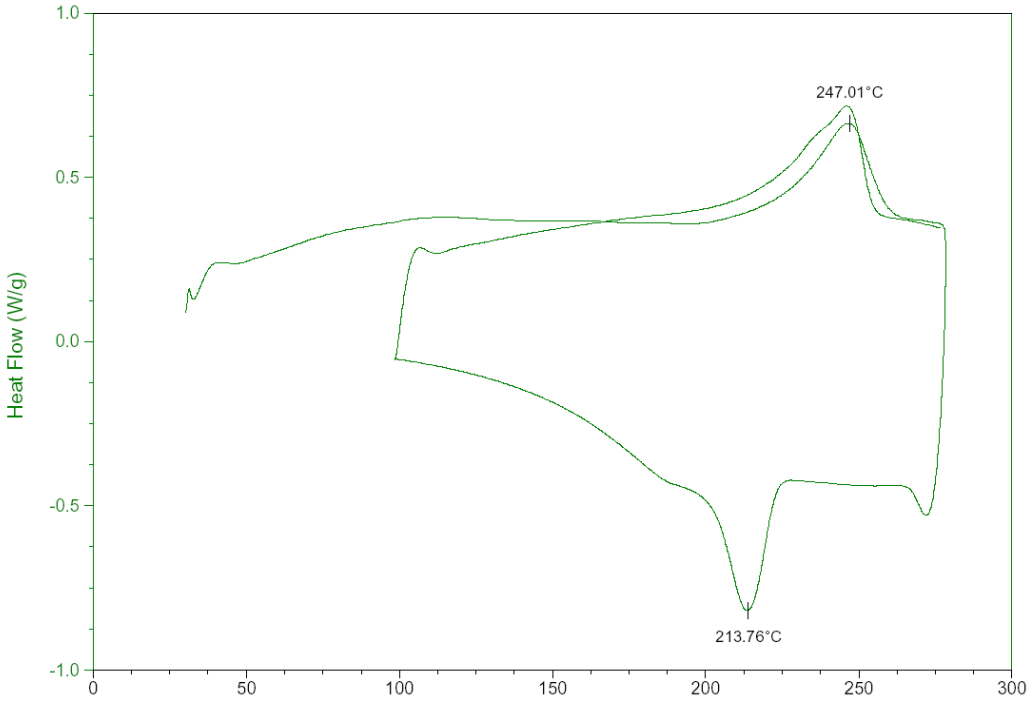

Figure A.6 DSC of 4% LiCl/nylon 66

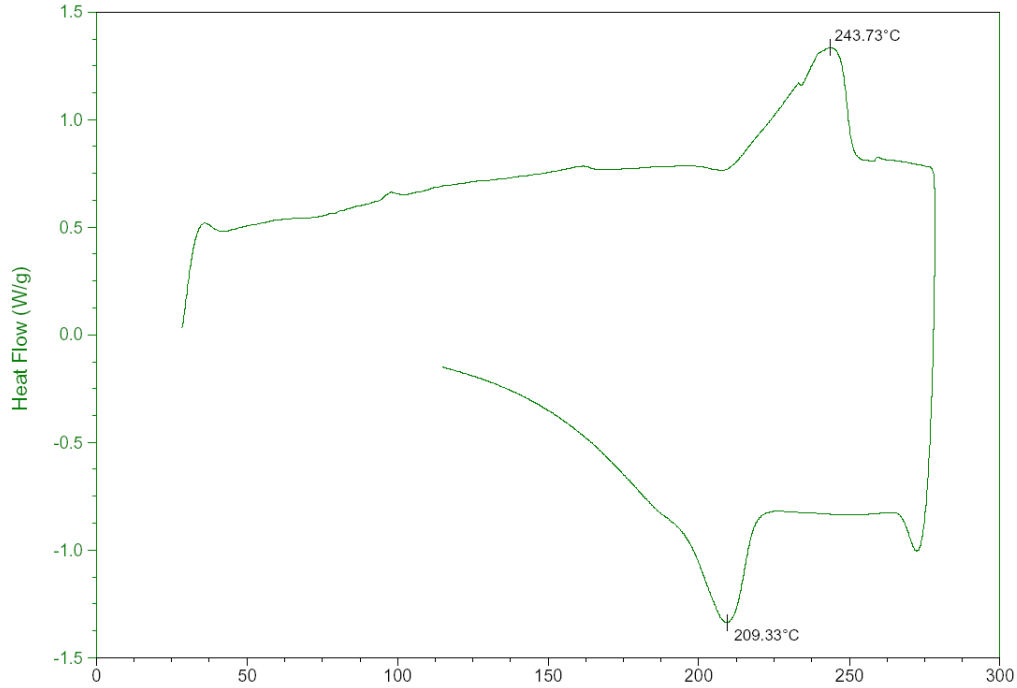

Figure A.7 DSC of 4% NBBSA/nylon 66

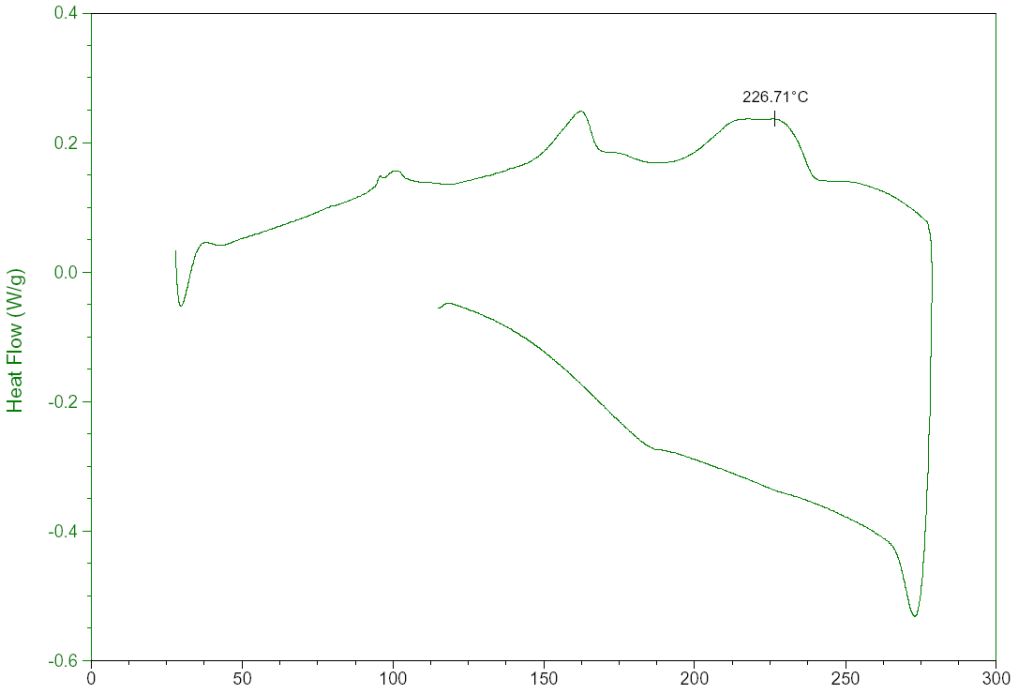

Figure A.8 DSC of 10% LiCl/nylon 66

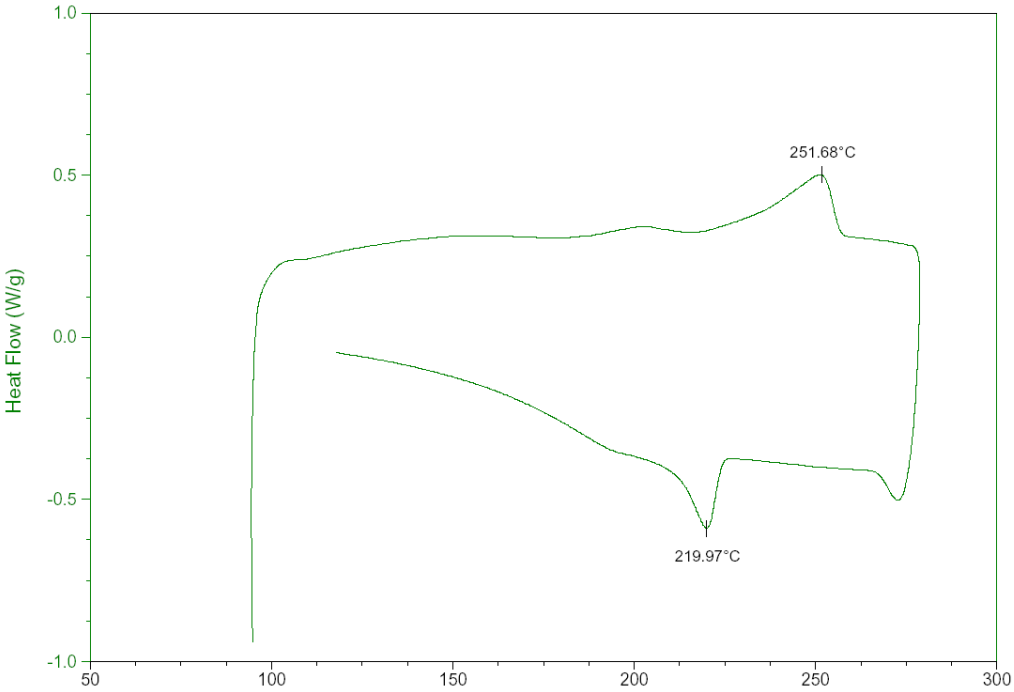

Figure A.9 DSC of 3% LiCl / 3% NBBSA / nylon 66

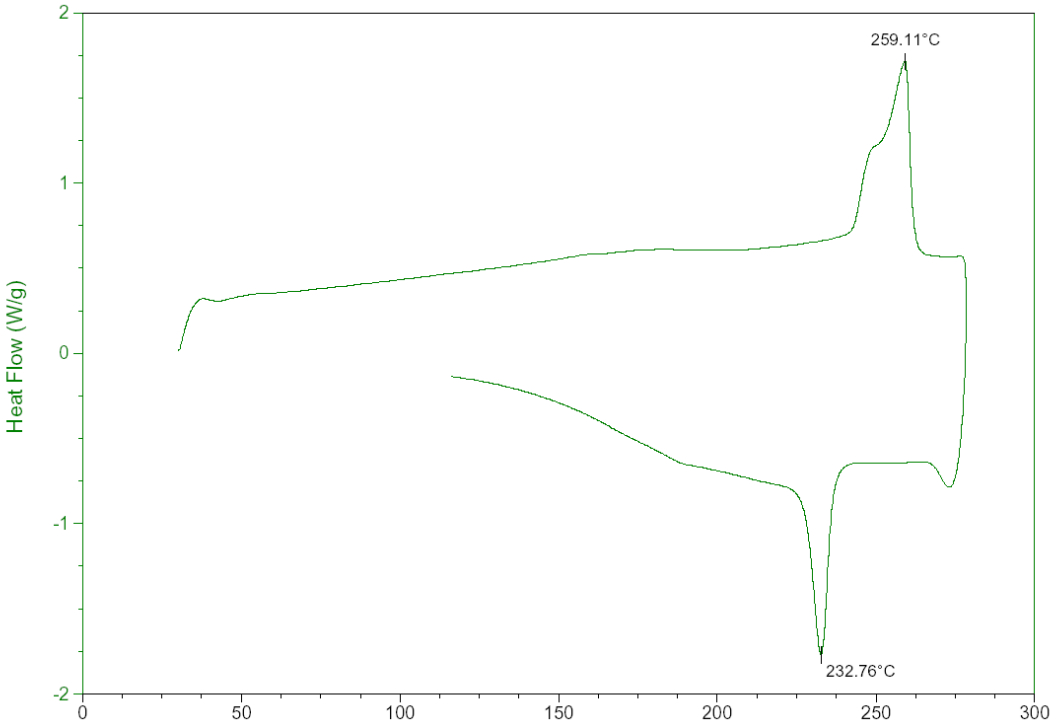

Figure A.10 DSC of 6% Theourea / nylon 66

APPENDIX B

MATLAB CODE USED FOR MECHANICAL MODELING

B.1 Halpin-Tsai Model

```
%---------Properties of matrix and fiber
Em=1.9;
dm=1.13;            %density of matrix
Eaf=93.1584;
Etf=5;
df=1.6;             %density of fiber

%---------calculation of volume fraction
wf=0.333;           %weight fraction of fiber
wm=1-wf;
dc=1/(wf/df+wm/dm); %calculated density of composites
vf=(dc-dm)/(df-dm); %volume fraction of fiber
vm=1-vf;

l=177;
d=20;

%---------calculation of modulus
rE11=2*(l/d)+40*(vf^10);
yE11=((Eaf/Em)-1)/((Eaf/Em)+rE11);
E11=Em*(1+rE11*yE11*vf)/(1-yE11*vf);

rE22=2+40*(vf^10);
yE22=((Etf/Em)-1)/((Etf/Em)+rE22);
E22=Em*(1+rE22*yE22*vf)/(1-yE22*vf);

E=(3*E11+5*E22)/8
```

B.2 Cox model

```
%---------Properties of matrix and fiber
Em=1915;
sm=44;              %stength of matrix
Gm=1100;            %shear modulus of matrix
dm=1.13;            %density of matrix
Ef=120000;
sf=130;             %strength of fiber
df=1.6;             %density of fiber
```

```
%---------calculation of volume fraction
wf=0.133;           %weight fraction of fiber
wm=1-wf;
dc=1/(wf/df+wm/dm); %calculated density of composites
vf=(dc-dm)/(df-dm); %volume fraction of fiber
vm=1-vf;
la=0.153;
%---------interval among fibers
rf=0.01;            %radius of fiber
R=rf*(pi/vf)^0.5/2;

beta=(2*Gm/(Ef*rf*rf*log(R/rf)))^0.5;

n=23;               %number of different fiber length
l=[0.075, 0.125, 0.175, 0.225, 0.275, 0.325, 0.375, 0.425,
0.475, 0.525, 0.575, 0.625, 0.675, 0.725, 0.775, 0.825,
0.875, 0.975, 1.025, 1.125, 1.325, 1.475, 1.525];
                    %fiber length
x=[1282, 2109, 927, 227, 138, 113, 52, 44, 27, 21, 16, 4,
11, 8, 5, 3, 4, 1, 2, 2, 1, 1, 1]; %fiber length frequency

vn=0;               %total fiber volume (without multiply
the cross area)
for i=1:n
    vn=vn+x(i)*l(i);
end

for i=1:n
    vi(i)=x(i)*l(i)/vn;  %volume fraction of each length
end

for i=1:n
    alpha(i)=beta*l(i)/2;
    k(i)=(1-(tanh(alpha(i)))/alpha(i))*vi(i);
end

kl=0;
for i=1:n-1
    kl=kl+0.5*(k(i)+k(i+1))*(l(i+1)-l(i));
end
kl=kl/la;
k0=3/8;
E=kl*k0*Ef*vf+Em*vm
```

B.3 Kelly and Tyson

```
%---------Properties of matrix and fiber
Em=1915;
sm=44;              %stength of matrix
dm=1.13;            %density of matrix
Ef=64000;
sf=500;             %strength of fiber
df=1.6;             %density of fiber

%---------calculation of volume fraction
wf=0.4;             %weight fraction of fiber
wm=1-wf;
dc=1/(wf/df+wm/dm); %calculated density of composites
vf=(dc-dm)/(df-dm); %volume fraction of fiber
vm=1-vf;

tau=16;             %interfacial shear stress
d=0.02;             %diameter of fiber
lc=sm*d/(2*tau);    %critical fiber length

%---------input fiber length distribution
%---------10%
n=23;               %number of different fiber length
l=[0.075, 0.125, 0.175, 0.225, 0.275, 0.325, 0.375, 0.425,
0.475, 0.525, 0.575, 0.625, 0.675, 0.725, 0.775, 0.825,
0.875, 0.975, 1.025, 1.125, 1.325, 1.475, 1.525];
                    %fiber length
x=[1282, 2109, 927, 227, 138, 113, 52, 44, 27, 21, 16, 4,
11, 8, 5, 3, 4, 1, 2, 2, 1, 1, 1]; %fiber length frequency

%---------30%
n=25;
l=[0.075, 0.125, 0.175, 0.225, 0.275, 0.325, 0.375, 0.425,
0.475, 0.525, 0.575, 0.625, 0.675, 0.725, 0.775, 0.825,
0.875, 0.925, 1.025, 1.075, 1.125, 1.225, 1.275, 1.525,
1.625];
x=[1114, 1802, 869, 284, 239, 252, 111, 97, 60, 41, 36, 28,
18, 22, 6, 4, 3, 3, 5, 1, 1, 1, 1, 1, 1];

%---------TC2500
n=36;
l=[0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5,
0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 1, 1.05,
1.1, 1.15, 1.2, 1.25, 1.3, 1.35, 1.4, 1.45, 1.5, 1.55, 1.6,
1.65, 1.7, 2.35, 4.15];
x=[913, 1130, 717, 311, 275, 324, 183, 191, 164, 116, 128,
93, 62, 96, 45, 54, 33, 37, 28, 17, 23, 17, 8, 8, 4, 2, 4,
4, 4, 2, 2, 1, 1, 1, 1, 1];
```

```
vn=0;               %total fiber volume (without multiply
the cross area)
for i=1:n
    vn=vn+x(i)*l(i);
end

for i=1:n
    vi(i)=x(i)*l(i)*vf/vn;    %volume fraction of each
length
end

%------------calculation of final stength of composites

sm=sf*Em/Ef;
sc=vm*sm;
for i=1:n
    if l(i)<lc
        sc=sc+vi(i)*sf*l(i)/(2*lc);
    end

    if l(i)>=lc
        sc=sc+vi(i)*sf*(1-lc/(2*l(i)));
    end
end

sc
```

B.4 Gray Value Calculation

```
A=imread('run 1-1.tif');      %input image
B=rgb2gray(A);                %transfer colorful image to
black and white image
figure, imshow(A),figure, imshow(B);

P=impixel(B)                  %gray value
```

APPENDIX C

STATISTICAL ANALYSIS RESULTS FROM MINITAB

CF/Nylon 6 Normal temperature

Two-way ANOVA: Tensile Modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	395847	395847	1.37	0.253
Fiber Content	2	20014924	10007462	34.62	0.000
Interaction	2	111149	55574	0.19	0.826
Error	24	6937795	289075		
Total	29	27459714			

S = 537.7 R-Sq = 74.73% R-Sq(adj) = 69.47%

Two-way ANOVA: Tensile Strength versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	0.359	0.3593	0.05	0.821
Fiber Content	2	47.920	23.9598	3.48	0.047
Interaction	2	108.799	54.3994	7.90	0.002
Error	24	165.219	6.8841		
Total	29	322.297			

S = 2.624 R-Sq = 48.74% R-Sq(adj) = 38.06%

Two-way ANOVA: Tensile strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1.1990	1.19896	7.49	0.011
Fiber Content	2	16.7134	8.35669	52.20	0.000
Interaction	2	0.5364	0.26820	1.68	0.208
Error	24	3.8424	0.16010		
Total	29	22.2912			

S = 0.4001 R-Sq = 82.76% R-Sq(adj) = 79.17%

CF/Nylon 6 Low temperature

Two-way ANOVA: tensile modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1705904	1705904	1.34	0.258
Fiber Content	2	19528586	9764293	7.68	0.003
Interaction	2	5328666	2664333	2.10	0.145
Error	24	30501164	1270882		
Total	29	57064319			

S = 1127 R-Sq = 46.55% R-Sq(adj) = 35.41%

Two-way ANOVA: tensile strength versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	2003.58	2003.58	71.14	0.000
Fiber Content	2	290.23	145.12	5.15	0.014
Interaction	2	578.24	289.12	10.27	0.001
Error	24	675.97	28.17		
Total	29	3548.02			

S = 5.307 R-Sq = 80.95% R-Sq(adj) = 76.98%

Two-way ANOVA: tensile strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1.4166	1.41662	5.82	0.024
Fiber Content	2	14.7889	7.39443	30.39	0.000
Interaction	2	1.1927	0.59633	2.45	0.107
Error	24	5.8392	0.24330		
Total	29	23.2373			

S = 0.4933 R-Sq = 74.87% R-Sq(adj) = 69.64%

3% INTEC/nylon 6/cellulose fiber

Two-way ANOVA: tensile modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1774982	1774982	17.59	0.001
Fiber Content	2	5060951	2530476	25.08	0.000
Interaction	2	973805	486902	4.83	0.021
Error	18	1816000	100889		
Total	23	9625738			

S = 317.6 R-Sq = 81.13% R-Sq(adj) = 75.89%

Two-way ANOVA: tensile strength versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1625.58	1625.58	67.50	0.000
Fiber Content	2	2.51	1.26	0.05	0.949
Interaction	2	481.77	240.88	10.00	0.001
Error	18	433.50	24.08		
Total	23	2543.36			

S = 4.907 R-Sq = 82.96% R-Sq(adj) = 78.22%

Two-way ANOVA: tensile strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	6.3547	6.35466	31.18	0.000
Fiber Content	2	3.2935	1.64674	8.08	0.003
Interaction	2	0.6122	0.30612	1.50	0.249
Error	18	3.6684	0.20380		
Total	23	13.9288			

S = 0.4514 R-Sq = 73.66% R-Sq(adj) = 66.35%

Nylon 66/cellulose fiber, low temperature

Two-way ANOVA: Tensile Modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	764496	764496	1.16	0.291
Fiber Content	2	6863816	3431908	5.23	0.013
Interaction	2	587940	293970	0.45	0.644
Error	24	15760903	656704		
Total	29	23977156			

S = 810.4 R-Sq = 34.27% R-Sq(adj) = 20.57%

Two-way ANOVA: Tensile Stress versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	768.04	768.04	17.63	0.000
Fiber Content	2	1633.89	816.94	18.76	0.000
Interaction	2	4615.69	2307.85	52.99	0.000
Error	24	1045.35	43.56		
Total	29	8062.98			

S = 6.600 R-Sq = 87.04% R-Sq(adj) = 84.33%

Two-way ANOVA: Tensile Strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1.4898	1.48982	45.12	0.000
Fiber Content	2	4.8835	2.44177	73.95	0.000
Interaction	2	5.9003	2.95014	89.35	0.000
Error	24	0.7925	0.03302		
Total	29	13.0661			

S = 0.1817 R-Sq = 93.94% R-Sq(adj) = 92.67%

5% INTEC/nylon 66/CF

Two-way ANOVA: tensile modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	111866	111866	0.53	0.474
Fiber Content	2	7602637	3801319	17.99	0.000
Interaction	2	198793	99396	0.47	0.630
Error	24	5070298	211262		
Total	29	12983594			

S = 459.6 R-Sq = 60.95% R-Sq(adj) = 52.81%

Two-way ANOVA: tensile strength versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	6088.29	6088.29	427.05	0.000
Fiber Content	2	80.07	40.04	2.81	0.080
Interaction	2	1431.33	715.67	50.20	0.000
Error	24	342.16	14.26		
Total	29	7941.85			

S = 3.776 R-Sq = 95.69% R-Sq(adj) = 94.79%

Two-way ANOVA: tensile strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	20.1915	20.1915	301.68	0.000
Fiber Content	2	4.1991	2.0996	31.37	0.000
Interaction	2	6.3760	3.1880	47.63	0.000
Error	24	1.6063	0.0669		
Total	29	32.3729			

S = 0.2587 R-Sq = 95.04% R-Sq(adj) = 94.00%

Two-way ANOVA: Tensile Modulus versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	4228	4228	0.03	0.855
Fiber Content	2	8528340	4264170	34.78	0.000
Interaction	2	2155532	1077766	8.79	0.002
Error	18	2206640	122591		
Total	23	12894740			

S = 350.1 R-Sq = 82.89% R-Sq(adj) = 78.13%

Two-way ANOVA: Tensile Strength versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	2986.13	2986.13	68.94	0.000
Fiber Content	2	1520.85	760.42	17.55	0.000
Interaction	2	69.50	34.75	0.80	0.464
Error	18	779.71	43.32		
Total	23	5356.18			

S = 6.582 R-Sq = 85.44% R-Sq(adj) = 81.40%

Two-way ANOVA: Tensile Strain versus Molding Method, Fiber Content

Source	DF	SS	MS	F	P
Molding Method	1	1.85753	1.85753	34.21	0.000
Fiber Content	2	3.23196	1.61598	29.76	0.000
Interaction	2	0.20395	0.10198	1.88	0.182
Error	18	0.97740	0.05430		
Total	23	6.27083			

S = 0.2330 R-Sq = 84.41% R-Sq(adj) = 80.08%

CF/nylon 6 low temperature vs. normal temperature Injection Molding

General Linear Model: tensile modulus versus temperature

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	23178363	22450059	22450059	186.87	0.000
temperature	1	105326	105326	105326	0.88	0.357
Error	27	3243707	3243707	120137		
Total	29	26527395				

S = 346.608 R-Sq = 87.77% R-Sq(adj) = 86.87%

Term	Coef	SE Coef	T	P
Constant	2009.5	183.0	10.98	0.000
fiber conten	8882.0	649.7	13.67	0.000

General Linear Model: tensile stress versus temperature

Analysis of Variance for tensile stress, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	277.38	142.72	142.72	20.85	0.000
temperature	1	266.26	266.26	266.26	38.90	0.000
Error	27	184.82	184.82	6.85		
Total	29	728.46				

S = 2.61635 R-Sq = 74.63% R-Sq(adj) = 72.75%

Term	Coef	SE Coef	T	P
Constant	50.186	1.382	36.32	0.000
fiber conten	22.395	4.905	4.57	0.000

General Linear Model: tensile strain versus temperature

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	10.5328	10.0074	10.0074	31.95	0.000
temperature	1	0.0098	0.0098	0.0098	0.03	0.861

Error	27	8.4570	8.4570	0.3132
Total	29	18.9995		

S = 0.559663 R-Sq = 55.49% R-Sq(adj) = 52.19%

Term	Coef	SE Coef	T	P
Constant	3.7998	0.2955	12.86	0.000
fiber conten	-5.930	1.049	-5.65	0.000

General Linear Model: flexural modulus versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	15682944	9703433	9703433	779.41	0.000
temperature	1	7859026	7859026	7859026	631.26	0.000
Error	27	336142	336142	12450		
Total	29	23878112				

S = 111.578 R-Sq = 98.59% R-Sq(adj) = 98.49%

Term	Coef	SE Coef	T	P
Constant	1195.50	58.92	20.29	0.000
fiber conten	5839.4	209.2	27.92	0.000

General Linear Model: flexural stress versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural stress, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P

fiber content	1	3811.1	2839.5	2839.5	287.68	0.000
temperature	1	632.5	632.5	632.5	64.09	0.000
Error	27	266.5	266.5	9.9		
Total	29	4710.2				

S = 3.14171 R-Sq = 94.34% R-Sq(adj) = 93.92%

Term	Coef	SE Coef	T	P
Constant	65.290	1.659	39.35	0.000
fiber conten	99.891	5.889	16.96	0.000

CF/nylon 6 low temperature vs. normal temperature Compression Molding

General Linear Model: tensile modulus versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	10822317	11401793	11401793	6.97	0.014
temperature	1	588760	588760	588760	0.36	0.554
Error	27	44178212	44178212	1636230		
Total	29	55589288				

S = 1279.15 R-Sq = 20.53% R-Sq(adj) = 14.64%

Term	Coef	SE Coef	T	P
Constant	2356.4	675.5	3.49	0.002
fiber conten	6330	2398	2.64	0.014

General Linear Model: tensile strength versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	875.02	571.85	571.85	15.97	0.000
temperature	1	338.82	338.82	338.82	9.46	0.005
Error	27	966.91	966.91	35.81		
Total	29	2180.75				

S = 5.98428 R-Sq = 55.66% R-Sq(adj) = 52.38%

Term	Coef	SE Coef	T	P
Constant	59.892	3.160	18.95	0.000
fiber conten	-44.83	11.22	-4.00	0.000

General Linear Model: tensile strain versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	18.2745	17.3211	17.3211	75.62	0.000
temperature	1	0.0122	0.0122	0.0122	0.05	0.819
Error	27	6.1841	6.1841	0.2290		
Total	29	24.4708				

S = 0.478582 R-Sq = 74.73% R-Sq(adj) = 72.86%

Term	Coef	SE Coef	T	P
Constant	3.9057	0.2527	15.45	0.000
fiber conten	-7.8017	0.8971	-8.70	0.000

General Linear Model: flexural modulus versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	5139769	7579127	7579127	91.17	0.000
temperature	1	4842311	4842311	4842311	58.25	0.000
Error	27	2244672	2244672	83136		
Total	29	12226751				

S = 288.333 R-Sq = 81.64% R-Sq(adj) = 80.28%

Term	Coef	SE Coef	T	P
Constant	1661.6	152.3	10.91	0.000
fiber conten	5160.7	540.5	9.55	0.000

General Linear Model: flexural strength versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	404.87	157.33	157.33	1.74	0.198
temperature	1	736.10	736.10	736.10	8.14	0.008
Error	27	2441.78	2441.78	90.44		
Total	29	3582.75				

S = 9.50980 R-Sq = 31.85% R-Sq(adj) = 26.80%

Term	Coef	SE Coef	T	P
Constant	100.419	5.022	20.00	0.000
fiber conten	-23.51	17.83	-1.32	0.198

N6 low temp vs. 3% INTEC/N6 CM

General Linear Model: tensile modulus versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	3299148	3517942	3517942	26.51	0.000
temperature	1	251079	251079	251079	1.89	0.183
Error	21	2786979	2786979	132713		
Total	23	6337206				

S = 364.298 R-Sq = 56.02% R-Sq(adj) = 51.83%

Term	Coef	SE Coef	T	P
Constant	2505.0	235.4	10.64	0.000
fiber conten	4468.6	867.9	5.15	0.000

General Linear Model: tensile strength versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	544.51	510.69	510.69	25.11	0.000
temperature	1	5.01	5.01	5.01	0.25	0.625
Error	21	427.15	427.15	20.34		
Total	23	976.67				

S = 4.51005 R-Sq = 56.26% R-Sq(adj) = 52.10%

Term	Coef	SE Coef	T	P
Constant	60.626	2.914	20.81	0.000

```
fiber conten  -53.84    10.74  -5.01  0.000
```

General Linear Model: tensile strain versus temperature

```
Factor       Type   Levels  Values
temperature  fixed       2  0, 1


Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source         DF   Seq SS  Adj SS  Adj MS      F      P
fiber content   1   6.4911  8.5380  8.5380  26.12  0.000
temperature     1   2.3075  2.3075  2.3075   7.06  0.015
Error          21   6.8633  6.8633  0.3268
Total          23  15.6619


S = 0.571686   R-Sq = 56.18%   R-Sq(adj) = 52.00%


Term            Coef  SE Coef      T      P
Constant      3.3976   0.3694   9.20  0.000
fiber conten  -6.961    1.362  -5.11  0.000
```

General Linear Model: flexural modulus versus temperature

```
Factor       Type   Levels  Values
temperature  fixed       2  0, 1


Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source         DF   Seq SS   Adj SS   Adj MS      F      P
fiber content   1  4969615  6469304  6469304  62.21  0.000
temperature     1  1669460  1669460  1669460  16.05  0.001
Error          21  2183874  2183874   103994
Total          23  8822949


S = 322.481   R-Sq = 75.25%   R-Sq(adj) = 72.89%


Term            Coef  SE Coef     T      P
Constant      1309.0    208.3  6.28  0.000
```

fiber conten 6059.7   768.3 7.89 0.000

General Linear Model: flexural strength versus temperature

Factor   Type   Levels Values
temperature fixed   2 0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	0.2	3.0	3.0	0.03	0.871
temperature	1	12.8	12.8	12.8	0.12	0.737
Error	21	2307.6	2307.6	109.9		
Total	23	2320.6				

S = 10.4827   R-Sq = 0.56%   R-Sq(adj) = 0.00%

Term	Coef	SE Coef	T	P
Constant	88.904	6.773	13.13	0.000
fiber conten	4.10	24.97	0.16	0.871

N6 low temp vs. 3% INTEC/N6 IM

General Linear Model: tensile modulus versus temperature

Factor   Type   Levels Values
temperature fixed   2 0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	14866868	14508340	14508340	221.51	0.000
temperature	1	336176	336176	336176	5.13	0.034
Error	21	1375421	1375421	65496		
Total	23	16578465				

S = 255.922 R-Sq = 91.70% R-Sq(adj) = 90.91%

Term	Coef	SE Coef	T	P
Constant	1997.2	165.3	12.08	0.000
fiber conten	9074.7	609.7	14.88	0.000

General Linear Model: tensile strength versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	121.89	170.60	170.60	12.83	0.002
temperature	1	59.33	59.33	59.33	4.46	0.047
Error	21	279.34	279.34	13.30		
Total	23	460.56				

S = 3.64719 R-Sq = 39.35% R-Sq(adj) = 33.57%

Term	Coef	SE Coef	T	P
Constant	53.299	2.356	22.62	0.000
fiber conten	31.118	8.689	3.58	0.002

General Linear Model: tensile strain versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	7.3145	6.6891	6.6891	44.94	0.000
temperature	1	0.0280	0.0280	0.0280	0.19	0.669
Error	21	3.1255	3.1255	0.1488		
Total	23	10.4680				

S = 0.385787 R-Sq = 70.14% R-Sq(adj) = 67.30%

Term	Coef	SE Coef	T	P
Constant	3.9518	0.2492	15.85	0.000
fiber conten	-6.1618	0.9191	-6.70	0.000

General Linear Model: flexural modulus versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	7401407	7690682	7690682	554.39	0.000
temperature	1	421562	421562	421562	30.39	0.000
Error	21	291319	291319	13872		
Total	23	8114288				

S = 117.781 R-Sq = 96.41% R-Sq(adj) = 96.07%

Term	Coef	SE Coef	T	P
Constant	1671.78	76.10	21.97	0.000
fiber conten	6607.0	280.6	23.55	0.000

General Linear Model: flexural stress versus temperature

Factor	Type	Levels	Values
temperature	fixed	2	0, 1

Analysis of Variance for flexural stress, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	1019.88	1108.38	1108.38	94.19	0.000
temperature	1	93.95	93.95	93.95	7.98	0.010
Error	21	247.10	247.10	11.77		
Total	23	1360.93				

S = 3.43029 R-Sq = 81.84% R-Sq(adj) = 80.11%

Term	Coef	SE Coef	T	P
Constant	78.541	2.216	35.44	0.000
fiber conten	79.317	8.172	9.71	0.000

N66 Low temp vs. 5% INTEC/N66, IM

General Linear Model: tensile modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	4792222	4591717	4591717	10.98	0.003
treatment	1	348904	348904	348904	0.83	0.369
Error	27	11288647	11288647	418098		
Total	29	16429773				

S = 646.605 R-Sq = 31.29% R-Sq(adj) = 26.20%

Term	Coef	SE Coef	T	P
Constant	3263.4	314.6	10.37	0.000
fiber conten	4348	1312	3.31	0.003

General Linear Model: tensile strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	8935.0	5339.3	5339.3	131.10	0.000
treatment	1	83.3	83.3	83.3	2.04	0.164
Error	27	1099.6	1099.6	40.7		
Total	29	10117.9				

S = 6.38171 R-Sq = 89.13% R-Sq(adj) = 88.33%

Term	Coef	SE Coef	T	P
Constant	83.205	3.105	26.80	0.000
fiber conten	-148.28	12.95	-11.45	0.000

General Linear Model: tensile strain versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	31.240	20.405	20.405	465.53	0.000
treatment	1	0.036	0.036	0.036	0.82	0.373
Error	27	1.183	1.183	0.044		
Total	29	32.459				

S = 0.209360 R-Sq = 96.35% R-Sq(adj) = 96.08%

Term	Coef	SE Coef	T	P
Constant	3.9309	0.1019	38.59	0.000
fiber conten	-9.1663	0.4248	-21.58	0.000

General Linear Model: flexural modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	5512393	5817486	5817486	221.54	0.000
treatment	1	698833	698833	698833	26.61	0.000
Error	27	709006	709006	26259		
Total	29	6920232				

S = 162.048 R-Sq = 89.75% R-Sq(adj) = 89.00%

Term	Coef	SE Coef	T	P
Constant	2347.54	78.84	29.78	0.000
fiber conten	4894.4	328.8	14.88	0.000

General Linear Model: flexural strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	11651.4	7115.8	7115.8	62.29	0.000
treatment	1	77.4	77.4	77.4	0.68	0.418
Error	27	3084.4	3084.4	114.2		
Total	29	14813.2				

S = 10.6882 R-Sq = 79.18% R-Sq(adj) = 77.64%

Term	Coef	SE Coef	T	P
Constant	120.777	5.200	23.23	0.000
fiber conten	-171.17	21.69	-7.89	0.000

N66 low temp vs. 5% INTEC/N66, CM

General Linear Model: tensile modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	3931062	6465081	6465081	17.34	0.000
treatment	1	2580218	2580218	2580218	6.92	0.016
Error	21	7830932	7830932	372902		
Total	23	14342212				

S = 610.657 R-Sq = 45.40% R-Sq(adj) = 40.20%

Term	Coef	SE Coef	T	P
Constant	3040.0	332.2	9.15	0.000
fiber conten	5769	1385	4.16	0.000

General Linear Model: tensile strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	572.63	1097.23	1097.23	28.88	0.000
treatment	1	562.82	562.82	562.82	14.81	0.001
Error	21	797.92	797.92	38.00		
Total	23	1933.36				

S = 6.16409 R-Sq = 58.73% R-Sq(adj) = 54.80%

Term	Coef	SE Coef	T	P
Constant	16.460	3.353	4.91	0.000
fiber conten	75.15	13.98	5.37	0.000

General Linear Model: tensile strain versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	0.12383	0.21912	0.21912	6.12	0.022
treatment	1	0.09925	0.09925	0.09925	2.77	0.111
Error	21	0.75238	0.75238	0.03583		
Total	23	0.97546				

S = 0.189281 R-Sq = 22.87% R-Sq(adj) = 15.52%

Term	Coef	SE Coef	T	P
Constant	0.6961	0.1030	6.76	0.000
fiber conten	1.0620	0.4294	2.47	0.022

General Linear Model: flexural modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	1870868	3377073	3377073	32.90	0.000
treatment	1	1579841	1579841	1579841	15.39	0.001
Error	21	2155545	2155545	102645		
Total	23	5606254				

S = 320.383 R-Sq = 61.55% R-Sq(adj) = 57.89%

Term	Coef	SE Coef	T	P
Constant	2013.3	174.3	11.55	0.000
fiber conten	4169.2	726.9	5.74	0.000

General Linear Model: flexural strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	1345.3	6.7	6.7	0.03	0.872
treatment	1	2442.1	2442.1	2442.1	9.82	0.005
Error	21	5224.4	5224.4	248.8		
Total	23	9011.8				

S = 15.7728 R-Sq = 42.03% R-Sq(adj) = 36.51%

Term	Coef	SE Coef	T	P
Constant	83.537	8.579	9.74	0.000
fiber conten	-5.85	35.78	-0.16	0.872

5% INTEC/N66 vs. Plasticier/n66 CM

General Linear Model: tensile modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	7079294	7077071	7077071	21.98	0.000
treatment	1	1137	1137	1137	0.00	0.953
Error	21	6760584	6760584	321933		
Total	23	13841015				

S = 567.391 R-Sq = 51.16% R-Sq(adj) = 46.50%

Term	Coef	SE Coef	T	P
Constant	3260.6	264.9	12.31	0.000
fiber conten	6817	1454	4.69	0.000

General Linear Model: tensile strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	24.80	28.38	28.38	0.35	0.560
treatment	1	103.09	103.09	103.09	1.27	0.272
Error	21	1700.69	1700.69	80.99		
Total	23	1828.57				

S = 8.99917 R-Sq = 6.99% R-Sq(adj) = 0.00%

Term	Coef	SE Coef	T	P
Constant	30.150	4.202	7.18	0.000
fiber conten	13.65	23.06	0.59	0.560

General Linear Model: tensile strain versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	0.03769	0.03446	0.03446	0.39	0.540
treatment	1	0.05945	0.05945	0.05945	0.67	0.422
Error	21	1.86114	1.86114	0.08863		
Total	23	1.95828				

S = 0.297701 R-Sq = 4.96% R-Sq(adj) = 0.00%

Term	Coef	SE Coef	T	P
Constant	0.9718	0.1390	6.99	0.000
fiber conten	-0.4757	0.7628	-0.62	0.540

General Linear Model: flexural modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	2118946	2066483	2066483	23.14	0.000
treatment	1	251290	251290	251290	2.81	0.108
Error	21	1875359	1875359	89303		
Total	23	4245594				

S = 298.836 R-Sq = 55.83% R-Sq(adj) = 51.62%

Term	Coef	SE Coef	T	P
Constant	2504.1	139.5	17.95	0.000
fiber conten	3683.5	765.7	4.81	0.000

General Linear Model: flexural strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	2494.7	2463.7	2463.7	9.93	0.005
treatment	1	66.8	66.8	66.8	0.27	0.609
Error	21	5208.2	5208.2	248.0		
Total	23	7769.7				

S = 15.7483 R-Sq = 32.97% R-Sq(adj) = 26.58%

Term	Coef	SE Coef	T	P
Constant	113.612	7.353	15.45	0.000
fiber conten	-127.19	40.35	-3.15	0.005

5% INTEC/nylon 66 vs. plasticizer/nylon 66

General Linear Model: tensile modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	4780277	4674684	4674684	63.94	0.000
treatment	1	445161	445161	445161	6.09	0.022
Error	21	1535425	1535425	73115		
Total	23	6760863				

S = 270.399 R-Sq = 77.29% R-Sq(adj) = 75.13%

Term	Coef	SE Coef	T	P
Constant	3303.6	126.2	26.17	0.000
fiber conten	5540.2	692.9	8.00	0.000

General Linear Model: tensile strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	1525.96	1467.96	1467.96	50.36	0.000
treatment	1	444.65	444.65	444.65	15.25	0.001
Error	21	612.12	612.12	29.15		
Total	23	2582.73				

S = 5.39895 R-Sq = 76.30% R-Sq(adj) = 74.04%

Term	Coef	SE Coef	T	P
Constant	73.324	2.521	29.09	0.000
fiber conten	-98.18	13.83	-7.10	0.000

General Linear Model: tensile strain versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for tensile strain, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	10.1424	9.5442	9.5442	115.54	0.000
treatment	1	7.3578	7.3578	7.3578	89.07	0.000
Error	21	1.7347	1.7347	0.0826		
Total	23	19.2348				

S = 0.287409 R-Sq = 90.98% R-Sq(adj) = 90.12%

Term	Coef	SE Coef	T	P
Constant	3.2722	0.1342	24.38	0.000
fiber conten	-7.9163	0.7365	-10.75	0.000

General Linear Model: flexural modulus versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural modulus, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	5836041	5430977	5430977	105.94	0.000
treatment	1	5932874	5932874	5932874	115.73	0.000
Error	21	1076521	1076521	51263		
Total	23	12845437				

S = 226.413 R-Sq = 91.62% R-Sq(adj) = 90.82%

Term	Coef	SE Coef	T	P
Constant	2883.0	105.7	27.27	0.000
fiber conten	5971.6	580.2	10.29	0.000

General Linear Model: flexural strength versus treatment

Factor	Type	Levels	Values
treatment	fixed	2	0, 1

Analysis of Variance for flexural strength, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
fiber content	1	2841.6	3046.0	3046.0	30.80	0.000
treatment	1	3091.6	3091.6	3091.6	31.26	0.000
Error	21	2077.1	2077.1	98.9		
Total	23	8010.3				

S = 9.94530 R-Sq = 74.07% R-Sq(adj) = 71.60%

Term	Coef	SE Coef	T	P
Constant	130.476	4.643	28.10	0.000
fiber conten	-141.42	25.48	-5.55	0.000

APPENDIX D

STEPWISE REGRESSION RESULTS OF DESIGN OF EXPERIMENTS FROM MINITAB

Stepwise Regression: gray value versus A, B, ...

Alpha-to-Enter: 0.15 Alpha-to-Remove: 0.15

Response is gray value on 20 predictors, with N = 9

Step	1	2
Constant	200.1	404.1
C2	-0.00206	-0.00478
T-Value	-1.75	-5.41
P-Value	0.124	0.002
A		-0.305
T-Value		-4.35
P-Value		0.005
S	17.2	9.11
R-Sq	30.41	83.23
R-Sq(adj)	20.47	77.64

Stepwise Regression: temp 7 versus A, B, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is temp 7 on 20 predictors, with N = 9

Step	1	2
Constant	77.58	40.24
C	0.708	0.861
T-Value	10.83	20.17

P-Value	0.000	0.000
A2B		0.00001
T-Value		5.11
P-Value		0.002
S	2.27	1.06
R-Sq	94.37	98.95
R-Sq(adj)	93.57	98.60

Stepwise Regression: flexural modulus versus thickness, A, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is flexural modulus on 21 predictors, with N = 45

Step	1	2	3
Constant	4124	3480	1555
A	-3.65	-2.99	4.83
T-Value	-5.76	-4.76	2.10
P-Value	0.000	0.000	0.042
BC2		0.00087	0.00459
T-Value		2.89	4.19
P-Value		0.006	0.000
ABC2			-0.00002
T-Value			-3.50
P-Value			0.001
S	260	240	213
R-Sq	43.56	52.94	63.78
R-Sq(adj)	42.25	50.70	61.13

FM=1555+4.83A+0.00459BC2-0.00002ABC2

Stepwise Regression: flexural stength versus thickness, A, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is flexural stength on 21 predictors, with N = 45

Step	1	2	3

Constant	143.9	130.4	211.0
AC	-0.00083	-0.00078	-0.00086
T-Value	-5.50	-5.54	-6.49
P-Value	0.000	0.000	0.000
B2C		0.00034	0.00105
T-Value		2.80	3.94
P-Value		0.008	0.000
thickness			-648
T-Value			-2.93
P-Value			0.006
S	11.0	10.2	9.41
R-Sq	41.30	50.54	59.08
R-Sq(adj)	39.94	48.18	56.09

FS=211-0.00086AC+0.00105B2C-648t

Stepwise Regression: TS(SD) versus thickness, A, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is TS(Pa) on 21 predictors, with N = 9

Step	1
Constant	3050238
A2C	0.34
T-Value	3.37
P-Value	0.012
S	1952753
R-Sq	61.93
R-Sq(adj)	56.49

TS(SD)=3050238+0.34A2C

Stepwise Regression: torque*100 versus thickness, A, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is torque*100 on 21 predictors, with N = 9

Step	1	2
Constant	1062	4265
BC	1.94	1.82
T-Value	5.31	11.91
P-Value	0.001	0.000
AC2		-0.00024
T-Value		-5.92
P-Value		0.001
S	590	244
R-Sq	80.13	97.09
R-Sq(adj)	77.29	96.12

Torque=4265+1.82BC-0.00024AC2

Stepwise Regression: Die Temp versus thickness, A, ...

Alpha-to-Enter: 0.05 Alpha-to-Remove: 0.05

Response is Die Temp on 21 predictors, with N = 9

Step	1	2
Constant	22.32	-910.51
C	1.02	9.93
T-Value	8.90	5.68
P-Value	0.000	0.001
C2		-0.0212
T-Value		-5.10
P-Value		0.002
S	3.98	1.86
R-Sq	91.88	98.48
R-Sq(adj)	90.72	97.97